REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*
12-06-2007

2. REPORT TYPE
Final Technical Report

3. DATES COVERED *(From - To)*
May 1, 2001 - December 31, 2006

4. TITLE AND SUBTITLE
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

5a. CONTRACT NUMBER
N00014-01-1-0716

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research, Code 312
Ballston Centre Tower One
800 North Quincy Street
Arlington, VA 22217-5660

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Recognizing that native substrates are crucial for future development of III-nitride-based devices, this MURI investigated several approaches to III-nitride crystal growth: (1) growth of GaN from the vapor phase, (2) growth of GaN from the Na flux, (3) ammonothermal growth of GaN and (4) growth of AlN by sublimation. While all approaches generated important findings, the latter two processes have been developed the furthest and are currently being pursued commercially. Following basic studies of solubility and transport in the alkaline supercritical ammonia solutions, seeded growth of GaN has been achieved at rates exceeding 20 µm/day. The process is commercially appealing due to: simple equipment, scalability, high output volume and low growth temperature. Seeded growth of AlN has been achieved on SiC and AlN seeds. While growth on SiC enabled growth over large areas, it produced defective material with dislocation density in the 108 cm-2 range. In contrast, growth on spontaneously nucleated AlN seeds produced smaller but near perfect crystals with dislocations densities below 103 cm-2. Following these findings, an iterative scheme for gradual crystal expansion was developed, which allowed a diameter expansion of about 5 mm in each step. The quality and properties of grown single crystals were assessed by structural, optical, thermal and electrical characterization techniques.

15. SUBJECT TERMS
crystal growth, aluminum nitride, gallium nitride, sublimation, ammonothermal growth, continuum modeling

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclassified	Unclassified	Unclassified	Unlimited		Zlatko Sitar, Professor
					19b. TELEPHONE NUMBER *(Include area code)* 919.515.8637

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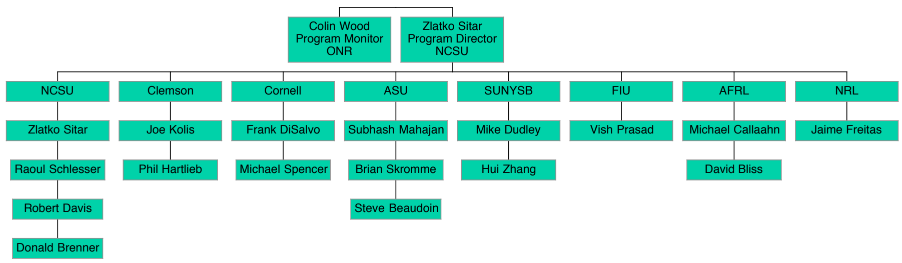
Organization of the team

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



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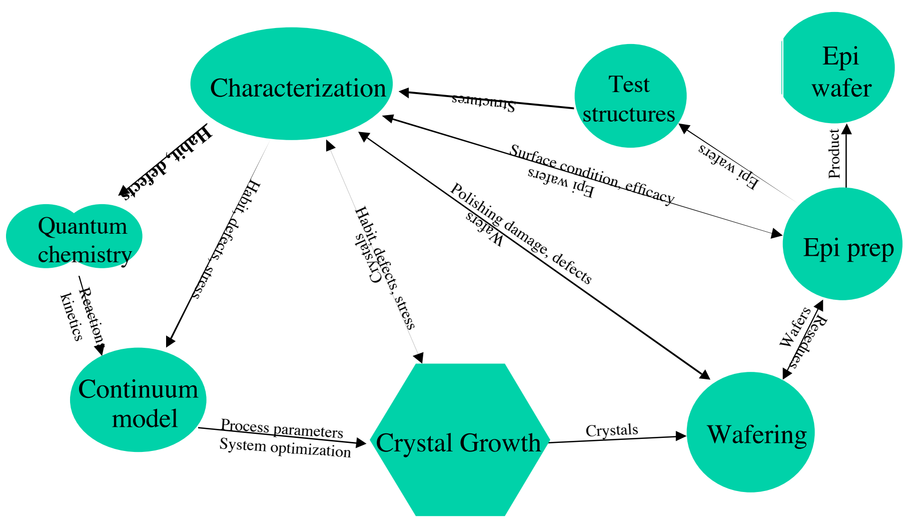
Project Components

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



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Ammonothermal Growth of III-Nitrides

Michael Callahan, Kelly Rakes, Buguo Wang
Air Force Research Laboratory,
Sensors Directorate, Hanscom AFB

Current Efforts

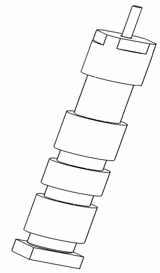
- Reduction of Wall Nucleation
- Reduction of oxygen and water in system
  - Use of Getters
  - High purity azides
  - Use of alkali salts (NaBr, KBr)
- Synthesis of InN and AlGaN alloys

Wall Nucleation Reduction / Abetment using temperature gradients and fluid flow

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Wall Nucleation Toolbox

1. **Temperature gradient**
2. **Heating configuration**
3. **Autoclave furniture/funnel design**



Work Done

- ☐ **Model Ideal Heating**
- ☐ **Model Ideal Furniture**
- ☐ **Experiment with Both**

Conclusions

•Some parasitic wall nucleation will occur even with optimal heating and furniture configurations

•Best way to control parasitic nucleation is modification of temperature profiles

• Modification of temperature profile adversely affects uniform crystallization on seeds by preventing formation of an isothermal zone

•Benefits of heating and furniture have not realized practicable gains

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Wall Nucleation Abetment by use of Sleeves

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

☐ Catalytic Properties of Nickel Autoclaves:

- Nickel is a known catalyst for growth of Nitrides and facilitates wall nucleation
- Use of materials that will not react with solvent and also have low affinity for GaN deposition will help reduce wall nucleation
- Molybdenum plates showed reduction in GaN nucleation over nickel plates in test experiment

☐ Solution:

- Line crystallization region with Molybdenum liners, seeds racks
- Designed and machined furniture but have not been tested
- Experiment with other materials i.e. Tungsten

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Erbium-doped Ammonothermal GaN crystals

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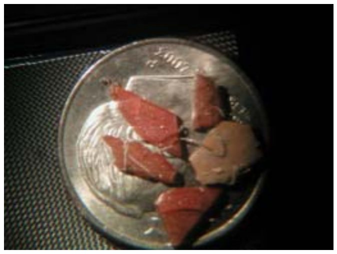

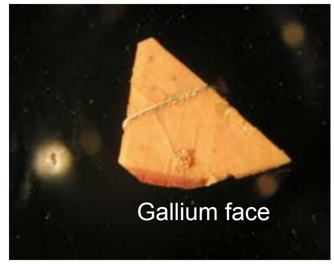

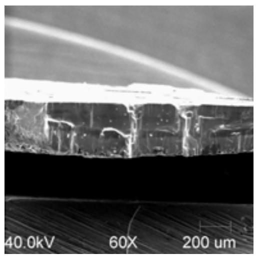

SEM cross section of polished sample

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IMPURITY Analysis of Erbium-doped run

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- Erbium incorporation ~ 100 ppma SIMS/GDMS
- Formation of Erbium Oxide at top of autoclave evidence successful of oxygen gettering
- Reduction ~ 5X of oxygen compared to runs not using erbium

Element (atoms/cc)	Ga face	N face
O	1×10^{19}	2×10^{19}
Si	1×10^{19}	5×10^{19}
C	2×10^{19}	2×10^{18}
Fe	2×10^{18}	1×10^{19}
Er	7×10^{17}	5×10^{18}

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Summary of Erbium doped runs

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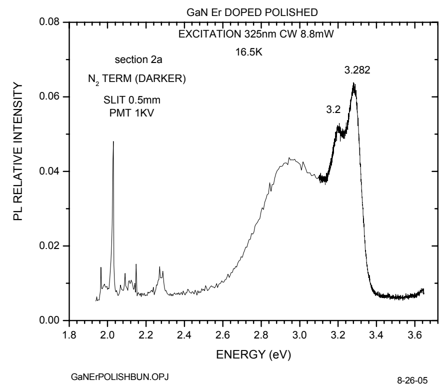
- GaN: Er metal mole ratio in autoclave - 5:2
- Nitrogen face growth rates > 50 µ µm/day
- Gallium face growth rates < 15 µm/day
- Total growth: 0.5-1mm on 5 HVPE seeds in single run !
- X-ray powder diffraction determined single crystal
  - Detected only (002) and (004) GaN peaks on both faces
- Rocking curves extremely broad > 3000 arcseconds
  - Nutrient was depleted: etch back evident on nitrogen face



Lines from the erbium transitions

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Ammonothermal synthesis of AlGaN and InN

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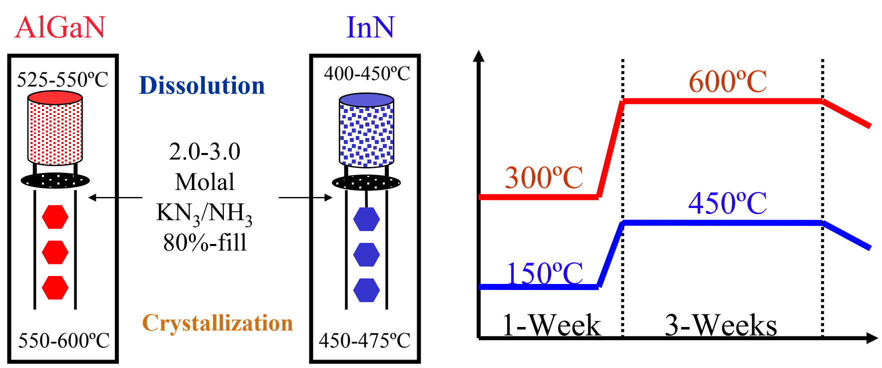

AlGaN and InN Retrograde soluble under conditions above

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PL of Polycrystalline Ammonothermal InN

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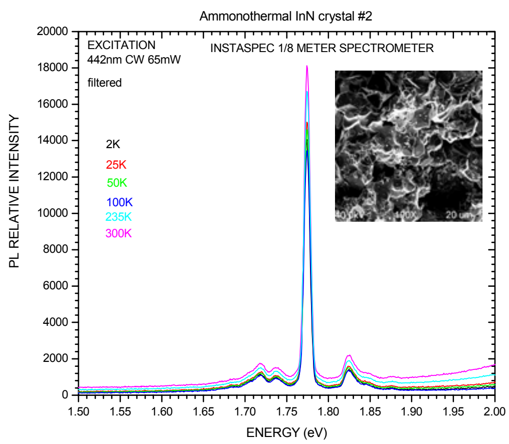

- Highly Contaminated with oxygen
- Band Edge @ ~1.7eV
- Growth Temp < 500° C !
- Technique looks promising for low defect InN substrates
- Growth on AlN seeds in progress
- In/Ni alloy formation evident

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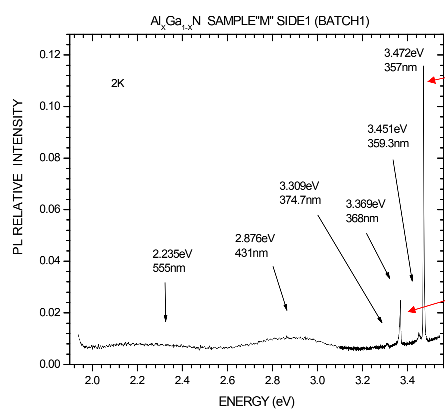
Pl of Ammono AlGaN grown on Polycrystalline GaN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



Pl from Ammono AlGaN growth

Over 50µm of AlGaN deposition

Pl from GaN seed

100 MeV shift from GaN bandgap, ~ 4% Al detected by EDS
Possibility of growing low defect AlGaN substrates !

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Oxygen Contamination

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Oxygen and water impurities now biggest remaining issue
  - Erbium and Rare Earths doping and gettering
    - Need to find optimal point of GaN/Er ratio for maximum oxygen gettering without distorting GaN lattice with Er incorporation
    - Investigate other getters
    - Gettering alone will not reduce oxygen to acceptable levels
  - Growth with Salts (NaBr)
    - GaN can be formed using Ga metal
      - Phase Issues need to be fully investigated
      - Rule out formation of cubic GaN inclusions
    - Can salts dissolve GaN nutrient ?
      - 1 experiment @ 525° C /2M NaBr result in no GaN dissolution

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Future Work

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Greater emphasis on initial growth to reduce defects at seed interface
  - Impurities should low enough level to obtain low defect material
  - Prevent nucleation, particulates on seeds during ramp up
    - Etch-back of seeds before growth
  - TEM analysis would aid in determination of causes for columnar growth and other defects
- Growth on cm^2 seeds in 2.2 cm and 3.4 cm autoclaves
- Further reduction of system impurities particularly water and oxygen

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Publications

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

1) "Synthesis of dense polycrystalline GaN of high purity by the chemical vapor reaction process", Buguo Wang, Michael Callahan, and John Bailey, J. Crystal Growth, 286 (2006) 50-54.
2) "GaN Single Crystals Grown on HVPE Seeds in Alkaline Supercritical Ammonia", M. Callahan, K. Rakes, D. Bliss, L. Bouthillette, M. Suscavage, B. Wang, and S-Q. Wang, Journal of Materials Science, 41 (2006) 1399-1407
3) "Ammonothermal Synthesis of III-Nitride Crystals", B. Wang and M. J. Callahan to Cryst. Growth & Design, in press
4) "Ammonothermal Synthesis of Aluminum Nitride Crystals ", B. Adekore, K. Rakes, B. Wang, M. Callahan, S. Pendurti, and Z. Sitar, J. Elect. Materials, in press
5) "Ammonothermal growth of GaN crystals in alkaline solutions" Buguo Wang, Michael J. Callahan, Kelly Rakes, David F. Bliss, Lionel O. Bouthillette, Sheng-Qi Wang, and Joseph W. Kolis, J. Crystal Growth, 287 (2006)376-380

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Modeling Ammonothermal Growth of GaN

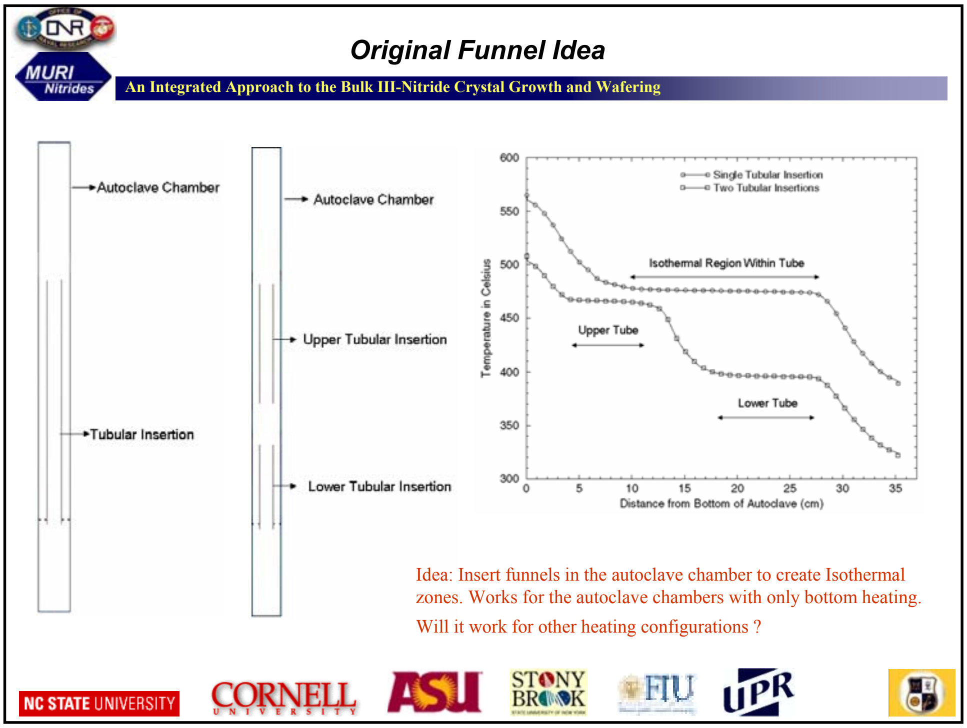
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

S. Pendurti and V. Prasad

Outline

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- *Funnel Idea*
- *Two Side Heater System*
- *Bottom Heater and One Side Heater*
- *Bottom Heater and Three Side Heaters*
- *Conclusion*
- *Summary*


Original Funnel Idea
MURI
Nitrides
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
Autoclave Chamber
Tubular Insertion
Autoclave Chamber
Upper Tubular Insertion
Lower Tubular Insertion
Single Tubular Insertion
Two Tubular Insertions
Isothermal Region Within Tube
Upper Tube
Lower Tube
Temperature in Celsius
Distance from Bottom of Autoclave (cm)
600
550
500
450
400
350
300
0
5
10
15
20
25
30
35
Idea: Insert funnels in the autoclave chamber to create Isothermal zones. Works for the autoclave chambers with only bottom heating.
Will it work for other heating configurations ?
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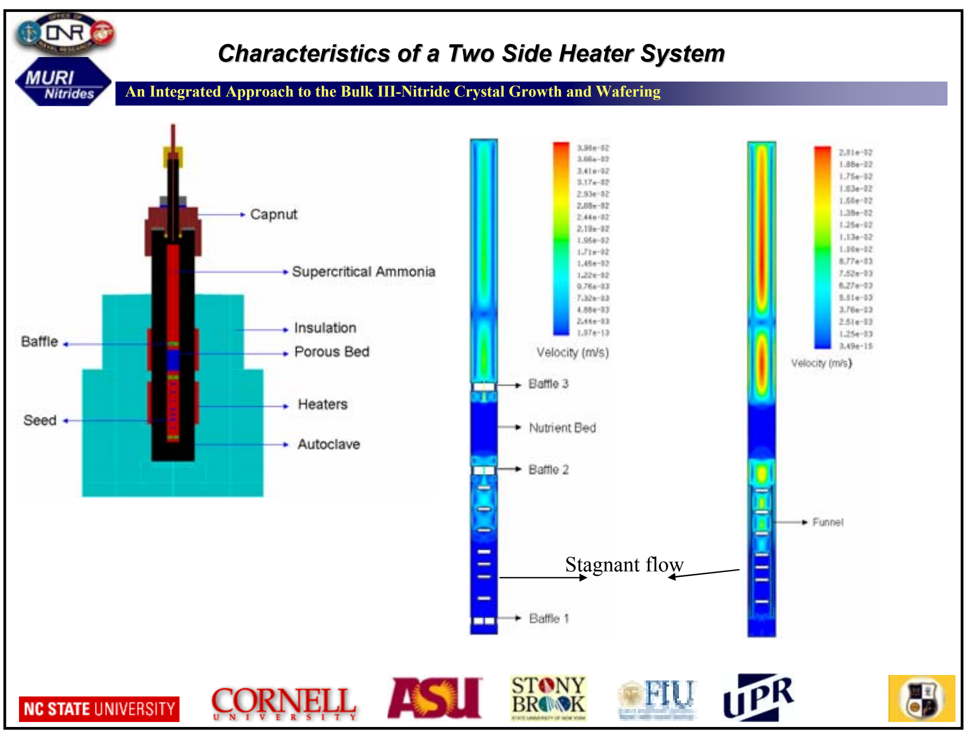
Characteristics of a Two Side Heater System
MURI
Nitrides
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
Capnut
Supercritical Ammonia
Insulation
Porous Bed
Heaters
Autoclave
Baffle
Seed
Velocity (m/s)
Baffle 3
Nutrient Bed
Baffle 2
Stagnant flow
Baffle 1
Velocity (m/s)
Funnel
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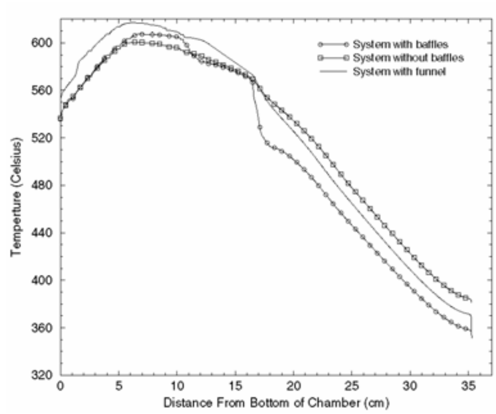
Characteristics of a Two Side Heater System

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

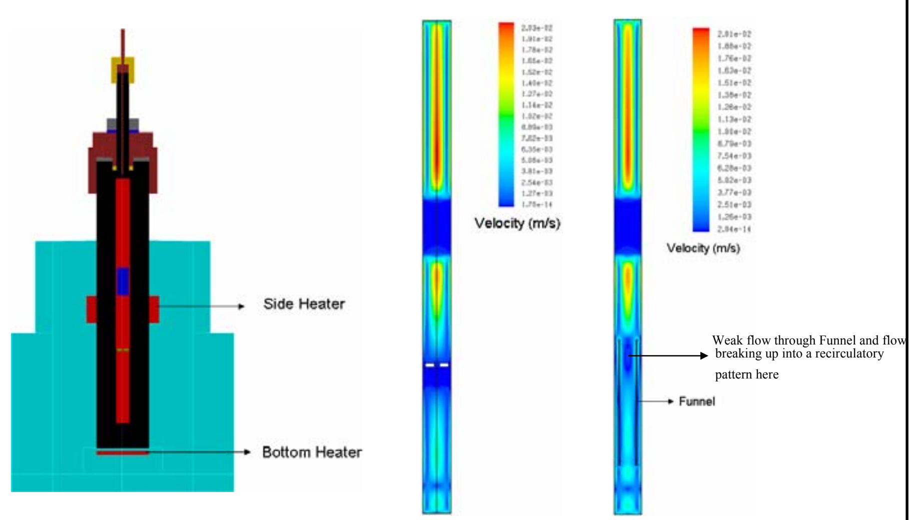


A funnel does not succeed in creating an isothermal lower growth region for a two side heater configuration. This is because of a stagnant layer of fluid and without any flow at the bottom of the autoclave chamber.

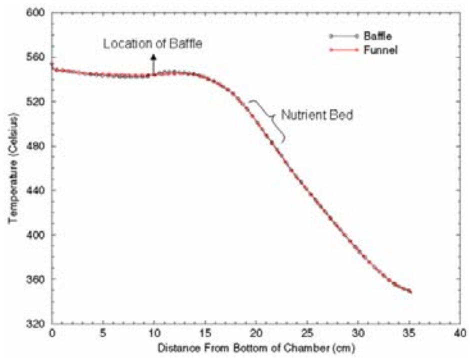
Calculations show, that funnel does not Make any difference for a two side heater configuration.

A Bottom Heater and One Side Heaters

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



	Lower Heater Power (254 W)	Upper Heater Power (310 W)	Bottom Thermocouple	Top Thermocouple
Modeling	560ºC	551ºC	521ºC	302ºC
Experimental	566ºC	550ºC	499ºC	309ºC

There is an isothermal growth zone with constant temperature both for cases with and without the funnel. The isothermal zone for the case without a funnel is fortuitous and is because of a particular set of heater power values

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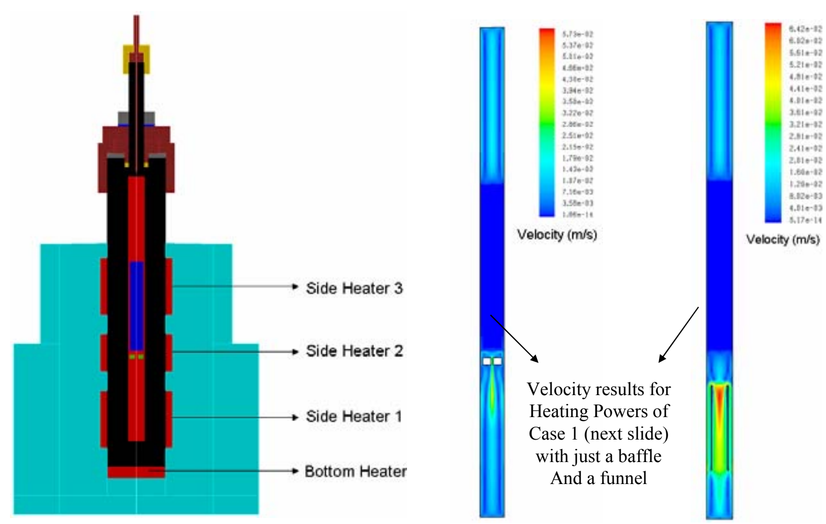
Bottom Heating with Three Side Heaters

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



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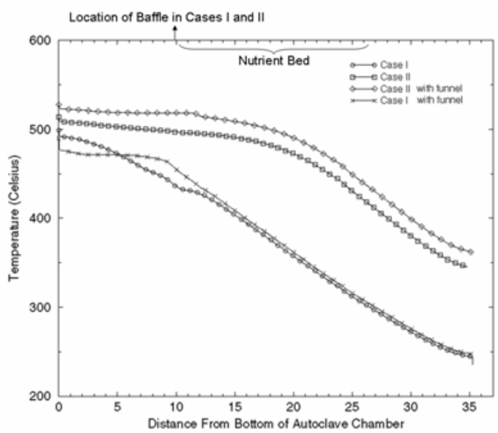
MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



Case 1: Bottom Heater Power is 279 W
Lowest Side Heater is 63 W
Middle Side Heater is 94 W
Top Side Heater is 261 W

Case 2: Bottom Heater Power is 153 W
Lowest Side Heater is 165 W
Middle Side Heater is 60 W
Top Side Heater is 40 W

	Bottom Heater	Upper Heater
Experiment	546^0C	504^0C
Modeling	535^oC	503^0C

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MURI Nitrides

Conclusion

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

For the bottom heater and three heater case, the funnel succeeds in creating isothermal growth zones at the bottom of the autoclave chamber, for both heater power settings applied in the experiments. However, the funnel concept does not seem to work for the two side heater case, while its effect is weaker for the bottom heater and one side heater for a particular set of heater power settings. This is related to the velocity fields. The velocity field has to be such that there is a constant flow from the inlet of the funnel to the outlet. If there is no flow (as in the two side heater configuration), or weak flow (one bottom heater, one side heater) with flow breaking up into recirculatory patterns the middle of the funnel, the funnel may not create an isothermal region. Hence a strong bottom heating and a lower side heater are needed to create forceful flow through the funnel.

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Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- *All heating configuration used in Hanscom have been explored, and a funnel tried out in them .*
- *Bottom heating, and lower side heater are necessary for the funnel to work*
- *Calculations on, with porous bed as exactly used in Hanscom.*

Acknowledgements

Kelly Rakes, Bumni Adekore, Michael Callahan.

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Raman Spectroscopy of Ammonothermal Growth Environment

James Perkins
Dr. Robert Nemanich
Dr. Zlatko Sitar
North Carolina State University

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Outline and Motivation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Raman Spectra of Neat Ammonia
  - Function of Temperature, Pressure, Density, and Time
  - Dissociation $2NH_3 \rightarrow N_2 + 3H_2$
  - Extent of Dimerization and H-Bonding
- NH_3 as a Solvent
  - Band Dependence on Association Strength with Ions
  - Perturbed Spectra of Solutes
- Determination of Intermediate Species

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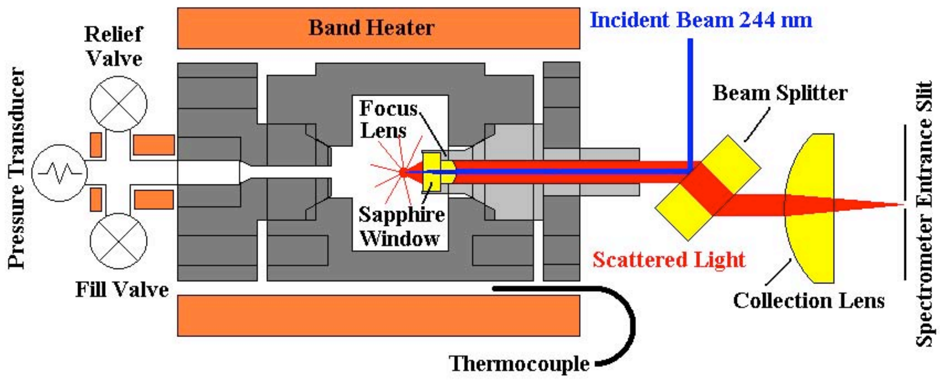
Experimental Setup

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- 13.5 ml autoclave
- tested to 1.2 kbar with ammonia

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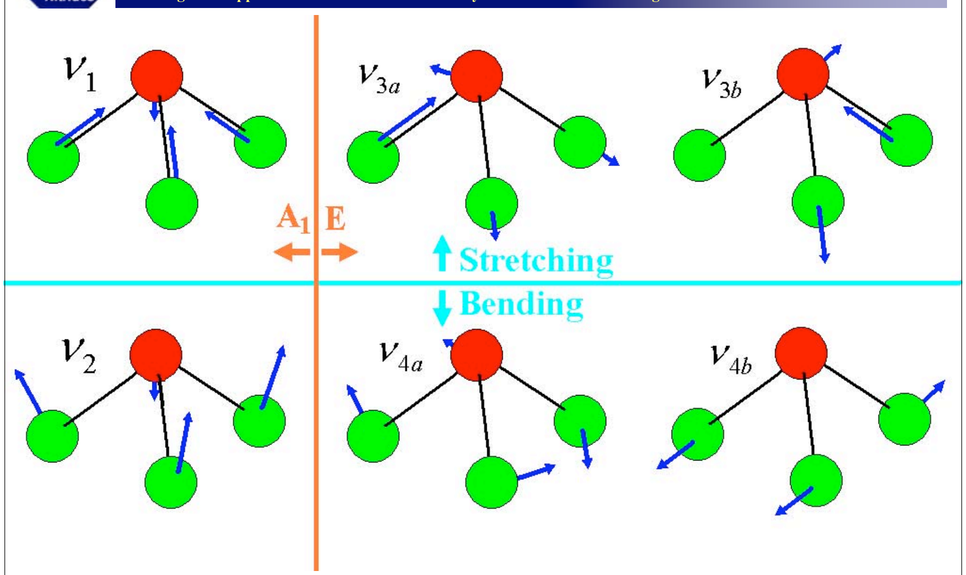
Normal Vibrations of NH_3

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



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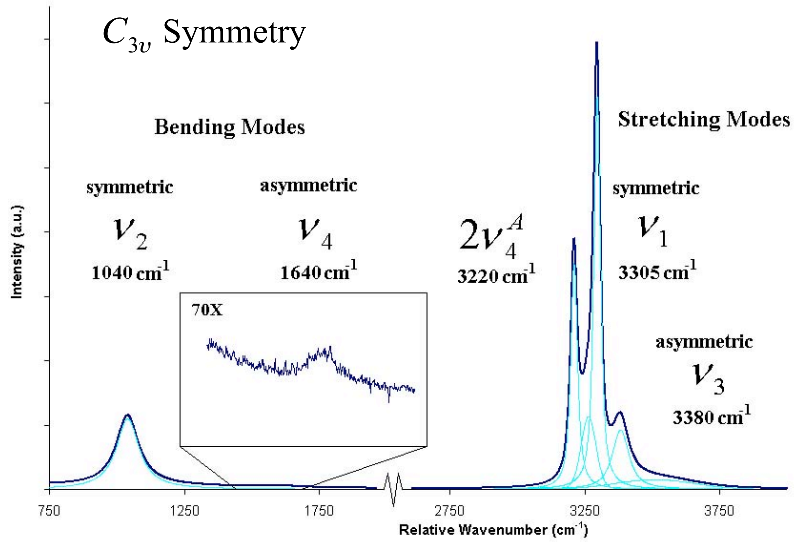
Raman Spectrum of Liquid Ammonia

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



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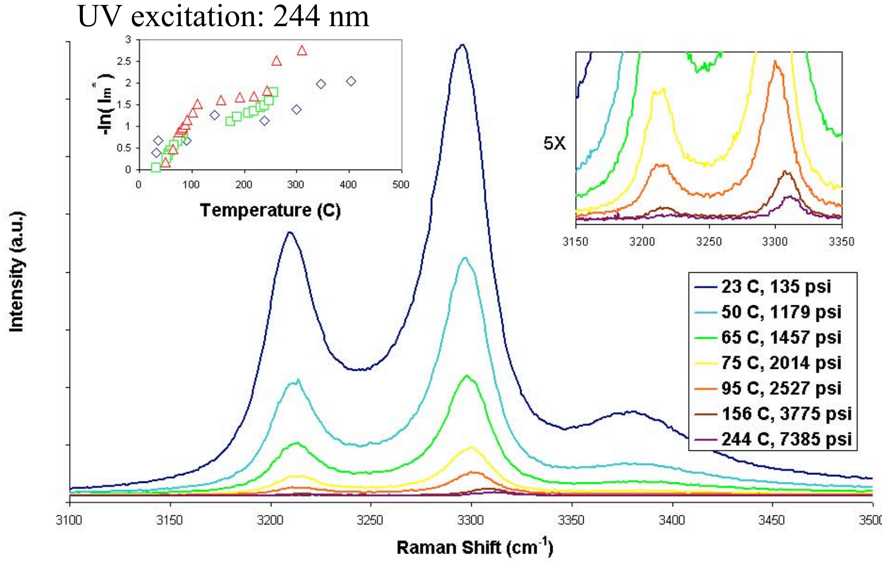
Raman Spectrum of Critical Ammonia

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

UV excitation: 244 nm



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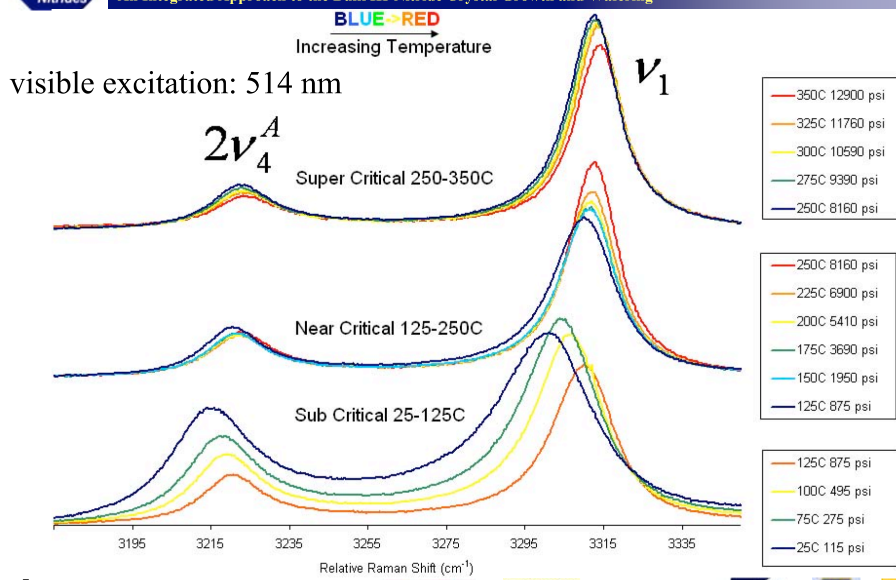
Visible Raman of Pure Ammonia

MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



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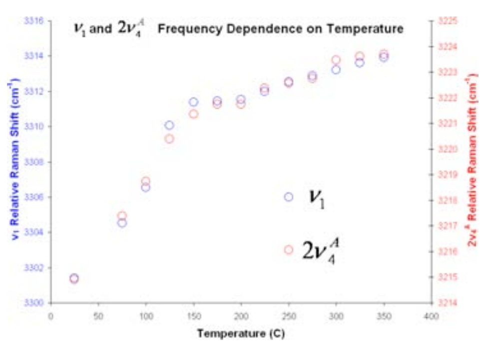
Summary and Ongoing Work

MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- Pure Ammonia Baseline for various fill percents found.
- No N_2 or H_2 signal observed.
- Longer duration (>1 day) studies on the horizon.
- Ready to add mineralizer and Gallium feedstock.

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Optical Characterization of III-Nitrides

B. J. Skromme and S. Sivasubramanian

Department of Electrical Engineering and
Center for Solid State Electronics Research
Arizona State University, Tempe, AZ 85287-5706

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Overview of Progress

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Reflectance & PL on ammonothermal ZnMgO (recent work)**
- **Reflectance of bulk AlN: Determination of the crystal-field splitting and valence band structure**
- **Optical characterization of bulk GaN grown by Na/Ga flux**
- **Structural-defect related PL in GaN: Folded prismatic faults in GaN/SiC**
- **Ion implantations to identify spectral fingerprints of various impurities in GaN (e.g., Cu, As, P, etc.) and study the origins of yellow PL in GaN**

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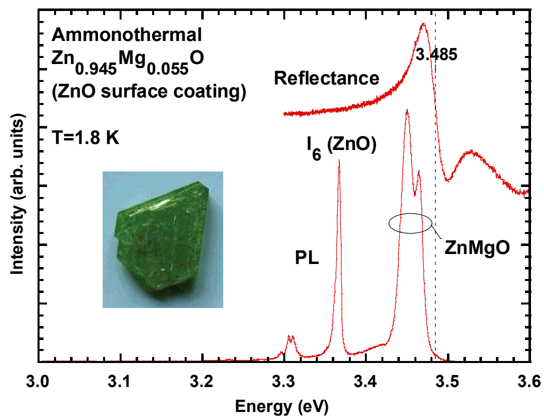
Reflectance and PL of Ammonothermal ZnMgO

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **ZnO 093 Growth conditions:** 90.5% ZnO, 9.5% MgO nutrients; 660° C; 0.9 Kbar; solvent is 4N KOH/0.5N LiOH; used ZnO seed.



- Reflectance/PL recorded from *c*-face
- ZnO formed during cooldown affects PL, not reflectance (probably patchy coating)
- Intrinsic exciton clearly observed in ZnMgO; PL peaks are probably bound excitons

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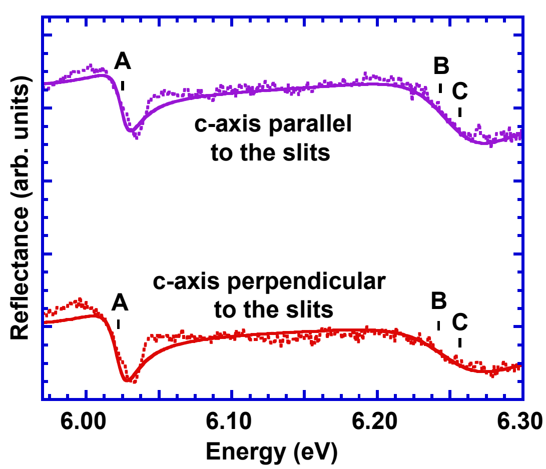
Reflectance of Bulk AlN Crystal

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Optical reflectance measurements of bulk AlN crystal #R407**



- R407 has a relatively flat *m*-plane face (see figure above)
- The relative oscillator strengths of the two features reverse when the sample is rotated 90º (partial polarization effects due to spectrometer gratings)
- Solid lines are theoretical fits to the data using a model dielectric function with three Lorentzian oscillators for the *A*, *B*, and *C* excitons, and an exciton-free dead layer at the surface

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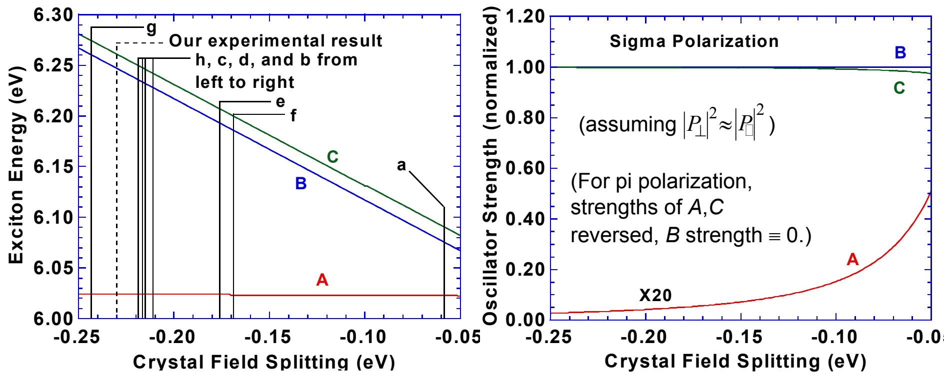
Theoretical Calculations for AlN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Exciton energies and oscillator strengths vary with crystal field splitting parameter (Δ_{cr}); theoretical calculations have yielded a range of values



Theoretical crystal field splitting calculations by: a) Suzuki *et al.*; b) Majewski *et al.*; c) Wei & Zunger; d) Kim *et al.*; e) Shimada *et al.*; f) Pugh *et al.*; g) Wagner & Bechstedt; h) Li *et al.* (listed in chronological order)

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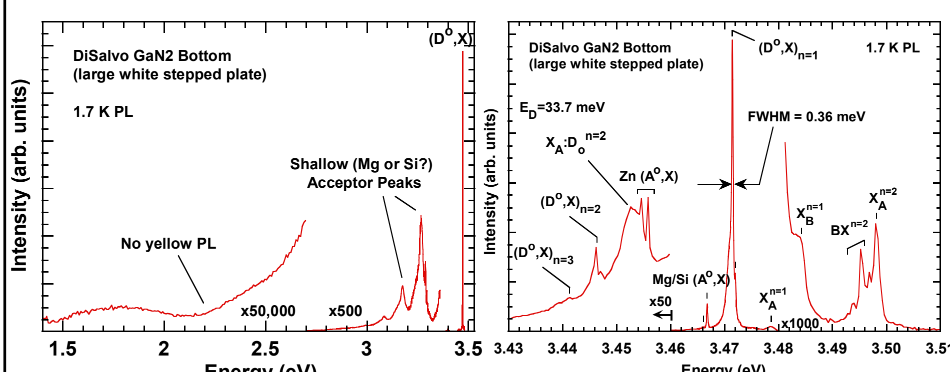
Na/Ga Flux Material

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Best Cornell sample studied (large white stepped plate) has (D°,X) FWHM of 0.36 meV, *extremely* weak deep level PL**



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Folded Prismatic Faults in GaN/SiC

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- We previously identified basal plane stacking faults as origins of ~3.4 eV PL peak in bulk ammonothermal GaN, and observed new ~3.2 eV peak in heteroepitaxial MOCVD GaN on SiC misoriented from [0001] towards the [11-20] direction (provided by R.F. Davis and collaborators)
- Prior TEM work by Dudley's group suggested the latter peak may be associated with folded I_1 basal plane/prismatic fault configurations and the associated stair-rod dislocations
- We have extended this study to use AFM, conductive AFM, and CL spectral imaging to study the intersections of these faults with the surface
- The results prove the electrically active nature of the faults and support the association of the 3.2 eV peak with these fault configurations (possibly with the lattice disconnections)

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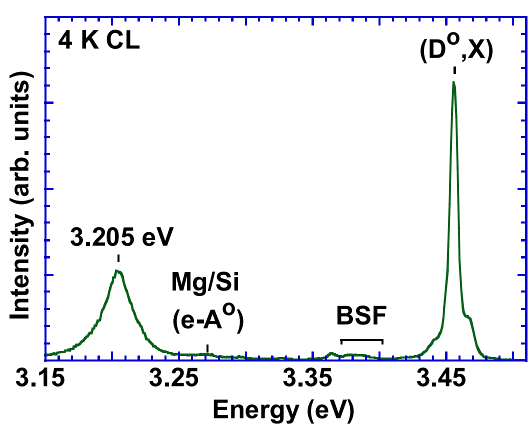
Folded Prismatic Faults in GaN/SiC

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- 1 μm GaN / 0.1 μm AlN / 6H-SiC tilted 3.5° from [0001] to [11-20]
- GaN grown by MOCVD at 1020 °C, AlN grown at 1100 °C
- 4 K CL spectrum on area showing folded faults intersecting surface



- 3.205 eV peak (and higher energy shoulder at ~3.225 eV, observed at higher temperature) believed uniquely related to folded fault configurations

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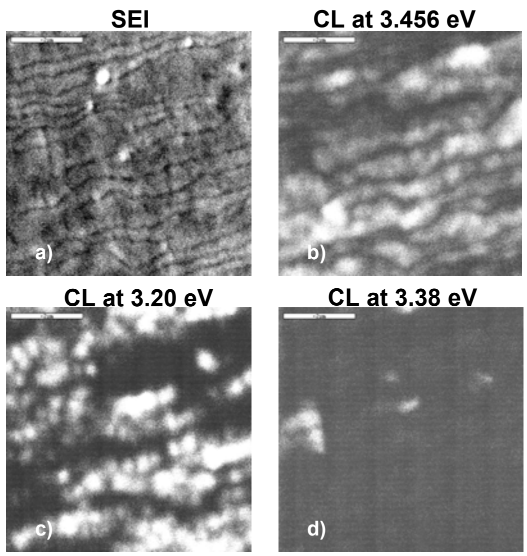
Folded Prismatic Faults in GaN/SiC

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- Secondary electron image reveals zigzagged lines where prismatic faults (PSFs) intersect surface
- Monochromatic CL image at 3.456 eV [(D^o,X) peak] is dark at positions of PSFs (competing processes)
- CL image at 3.20 eV is spotty, shows high intensity near the fault lines at specific locations believed to correspond to locations of stair-rod dislocations and lattice disconnections
- CL image at 3.38 eV shows a few bright spots possibly related to BSFs

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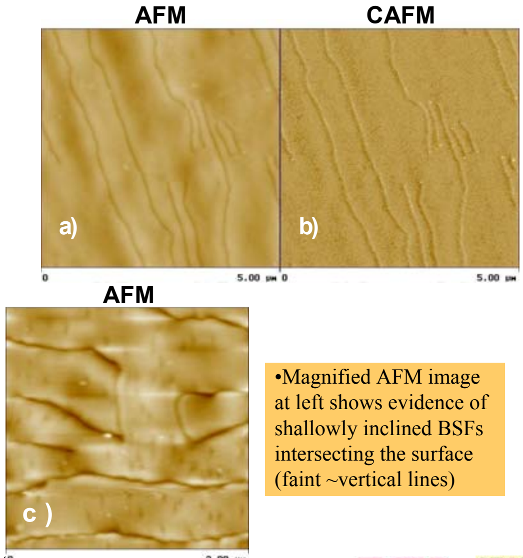
Folded Prismatic Faults in GaN/SiC

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- Atomic force microscopy (AFM) image (left) shows clear evidence of shallow (~3 nm deep) trenches corresponding to surface fault terminations
- Conductive AFM image (right) shows enhanced or reduced conductivity along the edges of the trenches, and enhanced conductivity (white spots) at the ends of each fault, where dislocations should be present
- First direct evidence for electrically active nature of these faults and associated dislocations; should impact device performance

- Magnified AFM image at left shows evidence of shallowly inclined BSFs intersecting the surface (faint ~vertical lines)

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Ion implanted HVPE GaN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Implantations performed to identify spectral fingerprints and behavior of various impurities in GaN
- Implanted species included Cu, to determine if it is electrically or optically active in GaN; As and P, to study the related isoelectronic centers; and various impurities including C, O, and N to study their effect on the yellow PL band in Ga

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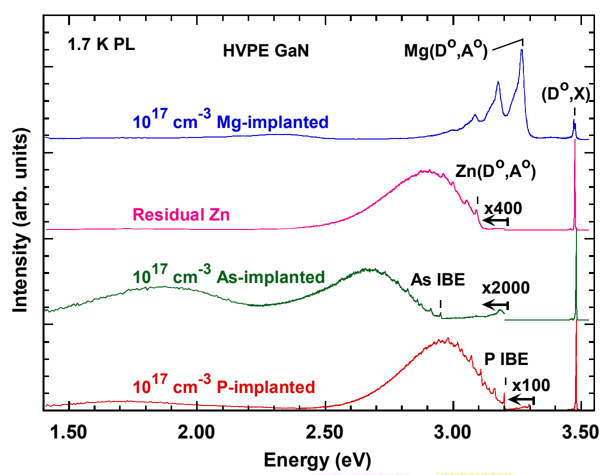
Ion Implantation Study Using HVPE GaN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Low temperature PL measurements of Mg, As, and P-implanted and residual Zn-doped HVPE GaN samples



As and P implants yield highly resolved spectra of isoelectronic-bound excitons with phonon replicas

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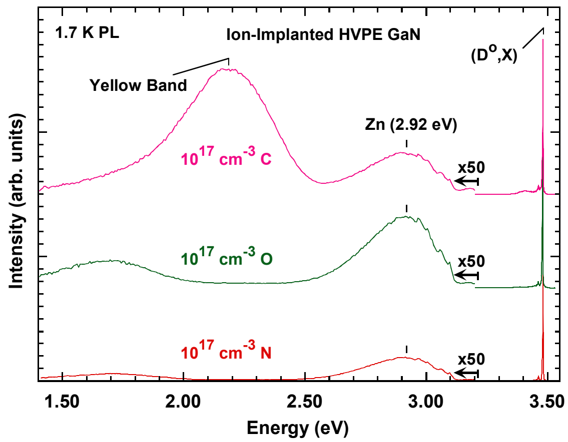
Ion Implantation in GaN: Yellow Band

MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **C-implanted HVPE GaN shows a strong enhancement of yellow (2.2 eV) luminescence band; *not* observed for N or O**



- May be more than one origin of yellow PL band (V_{Ga}-related, and also due to certain impurities?)
- Also studied PL properties of HVPE GaN implanted with Be, Mg, Zn, Cd, Ca, P, and As, and some co-implantations, to establish spectral "fingerprints" of various impurities

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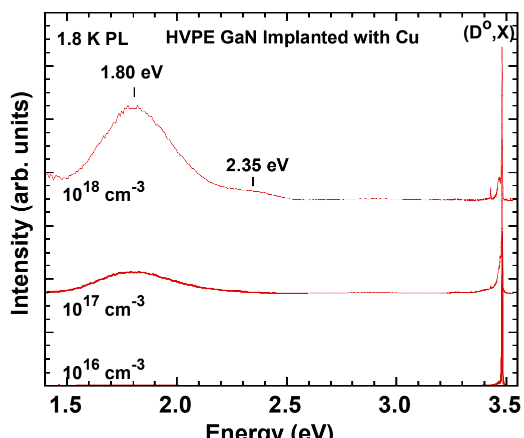
Ion implanted HVPE GaN

MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **All implants performed into high purity HVPE material from R. Molnar; samples capped after implantation with AlON and annealed for ~10 s at 1300 °C to remove damage, active dopants**



- Low T PL spectra of HVPE samples implanted with Cu at three doses
- 1.80 eV peak clearly enhanced by Cu implant; not by implants with any other species
- 2.35 eV peak normally enhanced only for *p*-type implants; suggests possible acceptor activity
- No clear excitonic features, although broad low energy shoulder observed on (D°,X) peak

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Accomplishments

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **First reflectance studies of ZnMgO, gave clear evidence of excitonic transitions in this system**
- **Determined crystal field splitting parameter of Δ_{cr} = -230 meV in unstrained bulk AlN, and characterized valence band splittings accurately for the first time in this material; selection rules have important implications for light-emitting devices in Al-rich AlGaN**
- **Characterized folded prismatic fault configurations in GaN using monochromatic CL imaging, AFM, and CAFM**
- **Found clear evidence associating 3.2 eV PL peak with specific locations along faults; 3.4 eV peak more generally associated with basal-plane faults**
- **Found first evidence for optical activity of Cu in GaN, in a 1.8 eV PL peak in Cu-implanted material. Identified clear isoelectronic behavior of As and P substituting for N, including site-switching behavior of P. Found that both C and Be enhance intensity of yellow PL, but not N, O, or other implants**

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MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Seeded Growth of AlN Single Crystals

Ziad G. Herro, Dejin Zhuang, Raoul Schlesser, Ramon Collazo, Rafael Dalmau and Zlatko Sitar

North Carolina State University

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MURI Nitrides

Outline

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Thermodynamics of crystal growth
  - Effect of the ambient gas on mass transport (N_2 versus Ar)
- Progress in seed and crystal quality
  - seed preparation
  - growth process optimization
  - crystal expansion
- Growth results and morphology
  - Growth along the c-direction (Al and N-face)
  - Effect of surface energy on growth morphology
- Conclusion

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Effect of the gas ambient on mass transport

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Thermodynamic consideration:**

  $AlN(s) = Al(g) + ½ N_2(g)$

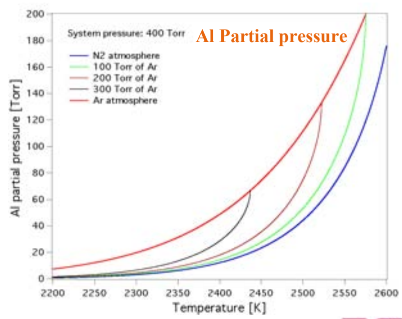
  $\Delta G = -RT \ln Kp$; $Kp = P_{Al} (P_{N2})^{1/2}$

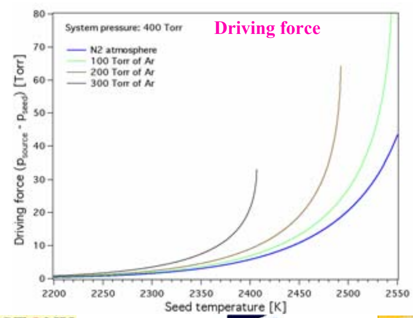
  $\ln Kp = -74719/T + 26.66$

  $P_{Al} = 2 P_{N2}$ (in vacuum/Ar atmosphere)

  $P_{sys} - P_{Ar} = P_{Al} + P_{N2}$ (in mixed atmosphere)

$$V_G = k' \cdot \frac{\exp\left[A - \frac{B}{T}\right]}{T^{1.2} \cdot P_T^{1.5}} \cdot \frac{\Delta T}{\delta}$$





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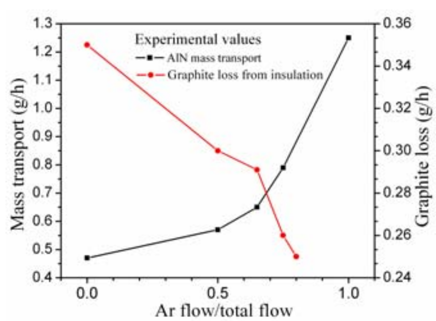
Effect of the gas ambient on transport rate

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Experimental verification:**

  Mass transport at different ratios of Ar flow/total flow



- The mass transport increases exponentially with increasing the Ar flow
- The use of Ar flow helps to reduce the graphite insulation degradation and the amount of C in the gas phase due to a reduced $C\text{-}N_2$ reaction

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Improvement of seed quality

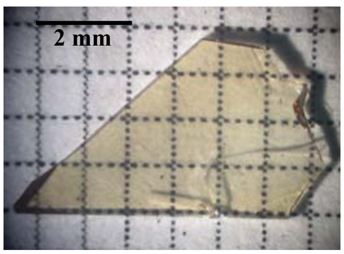
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

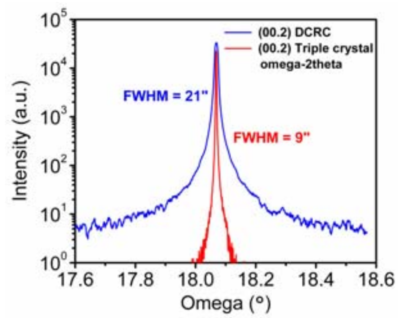
Seeded Growth

Results at the last MURI meeting

Seed from grain expansion

Crystal showing mirror-like and rough areas





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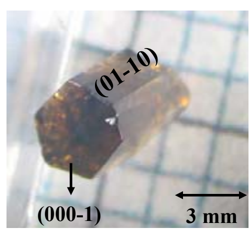
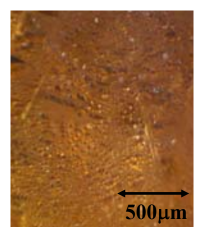
Growth of free-standing crystals

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Crystals nucleated on the top of source



Free standing crystal showing the *m* and *c*- facets



KOH etching on the *c*- facet revealing the N-polarity

- Freely nucleated crystals reveal the natural crystal habit of AlN
- The *m* and *c*- facets are naturally observed, thus revealing their stability
- Aqueous KOH etching (60ºC for 5 min) shows that all observed *c* facets are N-polar
- These crystals are excellent candidates for seeds

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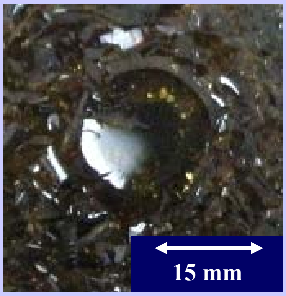
Improvement of crystal quality

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



Results at the last MURI meeting

- Photograph of a crystal, 15 mm in diameter and 12 mm in height, grown along the [002] direction from a 5 mm N-polar seed
  - A single, mirror-like facet is observed in the middle that covers nearly the whole monocrystalline area
  - Parasitic polycrystalline nucleation is confined around the central monocrystalline area

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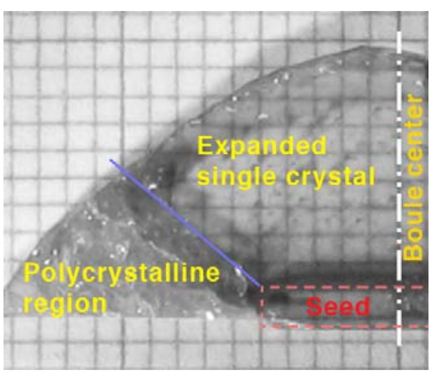
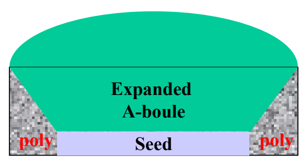
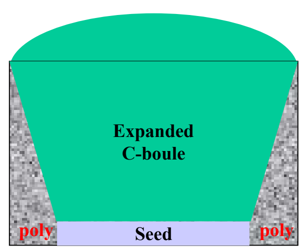
Crystal expansion angle

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering





- Expansion angle ~45°



- Expansion angle ~18-20°
- Good facet control

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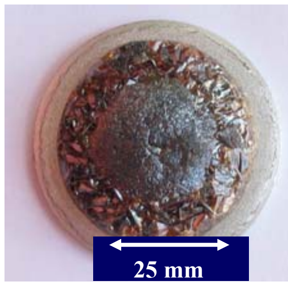
Effect of seed temperature

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



$T_{seed} < 2150°C$

$T_{seed} > 2150°C$

- Besides the seed quality, seed temperature is an important parameter to control to avoid surface roughness
  - Al_2O_3 and Al_4C_3 nucleate at low temperatures

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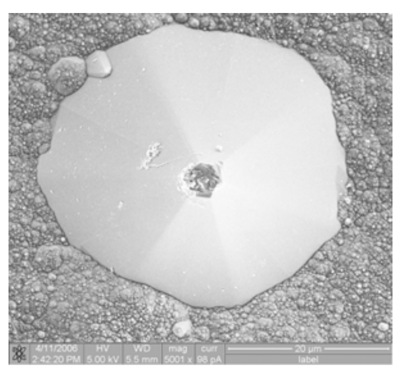
Wet etching

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Al-polar facet etched in KOH/NaOH eutectic at 430°C for 2 minutes
- Well defined hexagonal pits - defect etching
- EPD is about 2.5×10^4 cm^{-2}

- N-polar facet etched in 6M KOH solution at 60°C for 10 minutes
- Well defined hexagonal hillocks



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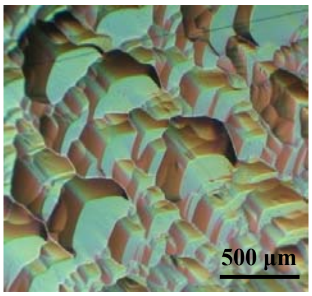
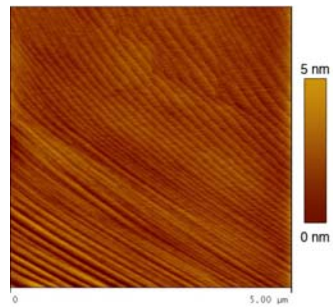
Growth on (002)-oriented seeds (Al-face)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Many growth centers are obvserved on as-grown crystal surfaces reflecting a rather high supersaturation
- Step height of about 1 lattice parameter unit (0.5 nm)
- Terrace width varies between 50 nm and 70 nm



Optical microscopy



AFM measurement

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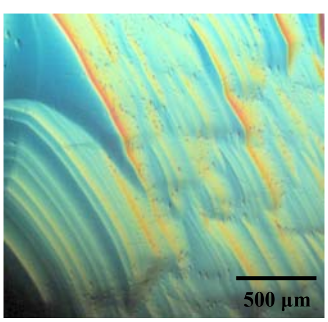
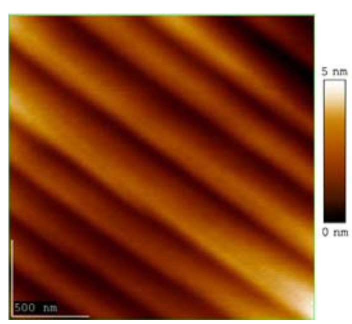
Growth on (002)-oriented seeds (N-face)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- One growth center controls the whole growth surface; step flow growth mechanism.
- Step height of about 1 lattice parameter unit (0.5 nm).
- Terrace width L varies between 200 nm and 250 nm.



Optical microscopy



AFM measurement

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Model for surface morphology difference

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- According to the BCF theory: $$L = 4\pi \frac{\gamma a}{kT \ln(1+\sigma)}$$

a is the lattice parameter, γ is the surface energy,

σ is the vapor supersaturation; $\sigma = \frac{P}{P_{eq}} - 1$ estimated to be around 2%

- As seen by the arriving Al species, N-polar (0001) surfaces have three dangling bonds while Al-polar surfaces have only one.
- $\gamma_N = 3\ \gamma_{Al}$, therefore $L_N = 3\ L_{Al}$, experimental results from AFM measurements agree with the theory.
- To have the same L in the case of Al-polarity as in N-polarity σ should be reduced to 0.6 %, leading to very low growth rates.

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Conclusion

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **The use of Ar as ambient gas**
  - **Implementation of an additional growth parameter**
  - **Increase the transport rate while keeping the same temperature, pressure and temperature gradient**
- **AlN boule growth**
  - **Very high quality (002)-seeds and (002)-crystals were obtained**
  - **Very uniform crystals having one single facet covering the whole area were obtained**
  - **Due to its high surface energy the N-polar face is very suitable for growth**

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

On the nature of the AlN surface oxide

Rafael Dalmau, Ramon Collazo, Seiji Mita, Zlatko Sitar
Department of Materials Science and Engineering
North Carolina State University

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Outline

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Polishing**
- **Oxide stability**
- **Surface analysis**
  - **Thermal evolution**
  - **Stoichiometry**
  - **Thickness**
- **Wet chemistry**
- **Summary**

Motivation: Demands of conventional AlN homoepitaxy place stringent requirements on bulk crystal surface preparation

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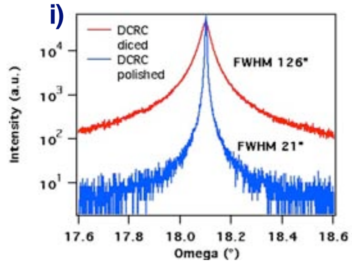
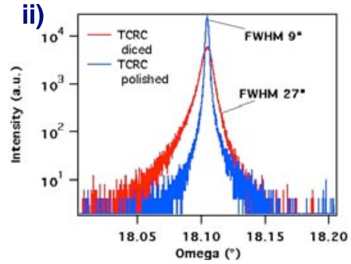
Polishing

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

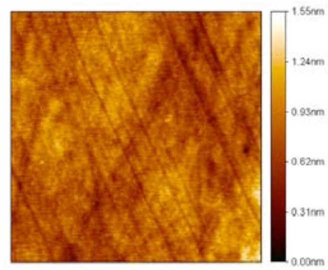
HRXRD (00.2) rocking curves:
i) double crystal
ii) triple crystal

i)


ii)


- HRXRD: polishing damage removal
- AFM: smooth surfaces
- Role of water?

AFM (2x2 μm^2) scan of polished AlN surface oriented ~ 2° off-axis from (00.2). RMS roughness: 0.152 nm.



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Driving force

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

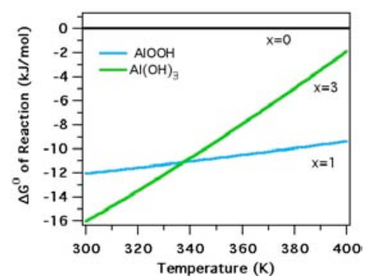
- What is the stable oxide on the AlN surface under atmospheric conditions?
- Consider stability of compounds:

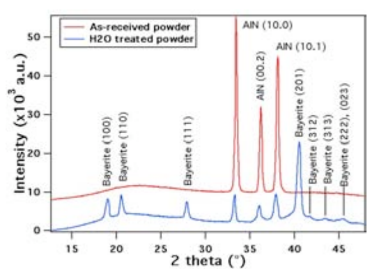
$$\alpha Al_2O_3 + x\,H_2O \leftrightarrow [Al_2O_3, x\,H_2O]$$

degree of hydration	compound
x = 0	aluminum oxide (Al_2O_3)
x = 1	aluminum oxide hydroxide (AlOOH)
x = 3	aluminum trihydroxide ($Al(OH)_3$)

- Reaction between H_2O and AlN is energetically favorable:

$$AlN + 2H_2O \rightarrow AlOOH_{amorph} + NH_3$$
$$AlOOH_{amorph} + H_2O \rightarrow Al(OH)_3$$
$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$





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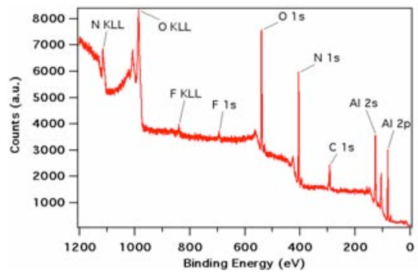
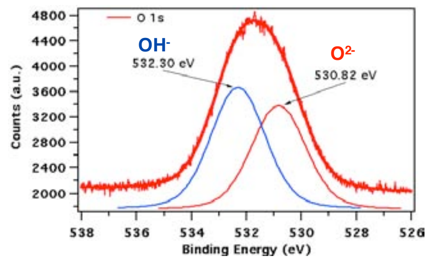
Surface analysis (XPS)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Surface sensitivity
- Molar concentration
- XPS survey scans
  - adventitious carbon
  - oxygen
- Deconvolution of O 1s envelope
  - OH^- bonding state
  - O^{2-} bonding state
  - ~1.5 eV peak separation
  - AlOOH





Tsuchida & Takahashi, J. Mater. Res. **9**(11), 2919 (1994)

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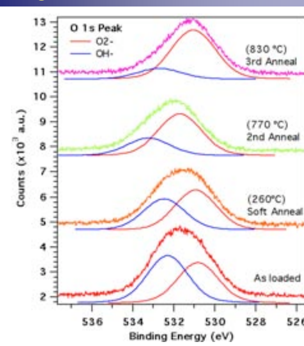
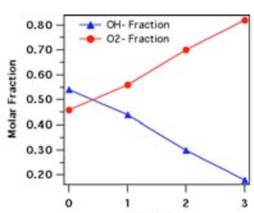
Thermal evolution

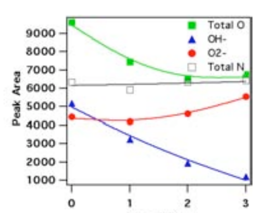
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

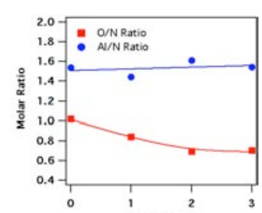
- UHV anneal ($1x10^{-9}$ Torr base pressure)
- Anneal steps
  0. As loaded
  1. 260 ºC
  2. 770 ºC
  3. 830 ºC

Surface behavior determined by Al









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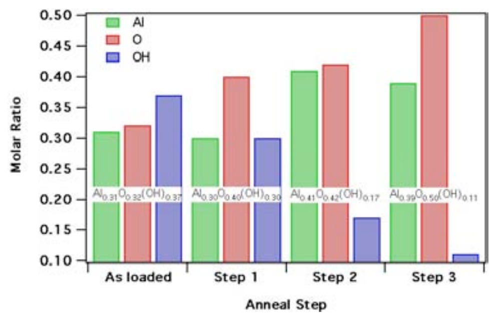
Hydroxide stoichiometry

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Calculations assumptions**
  - **no O-N reactions**
  - **stoichiometry Al:N = 1:1**
- **Ideal molar ratios**
  - **aluminum trihydroxide**
    - $Al_{0.25}(OH)_{0.75}$
  - **aluminum oxide hydroxide**
    - $Al_{0.33}O_{0.33}(OH)_{0.33}$
  - **aluminum oxide**
    - $Al_{0.4}O_{0.6}$

Overall thermal evolution
$AlOOH \Rightarrow Al_2O_3$

Transformation sequence



Plot of molar ratio of Al, O, and OH in surface oxides calculated from XPS spectra of AlN thin films: as-loaded; and annealed at 260, 770, and 830 °C (steps 1-3).

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Hydroxide thickness

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Estimated from intensity ratio of oxide and nitride contributions to Al 2p peak**

$$d^* = \lambda_o \sin\theta \ln\left[\frac{N_n \lambda_n}{N_o \lambda_o}\frac{I_o}{I_n} + 1\right]$$

sample	estimated thickness (nm)
air exposed AlN (minutes)	0.8
air exposed AlN (weeks)	1.2
hydrothermally treated AlN	> 6

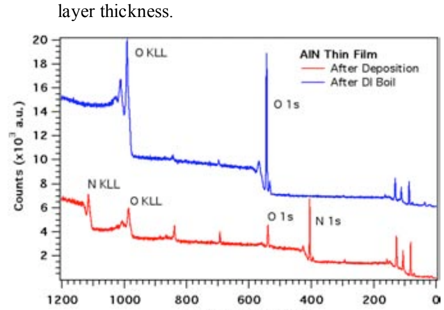
- **Hydrothermal treatment increases thickness**

* M. R. Alexander et al., Surf. Interf. Anal. **29**, 468 (2000)

Hydroxide growth

- DI H_2O boil (5 min)
- stoichiometric AlOOH

Hydrothermally treated AlN thin film.
XPS survey scans of AlN thin films before and after boiling in DI water. Note intensity increase of oxygen-related peaks and disappearance of N peaks after boiling, due to greater surface oxide layer thickness.



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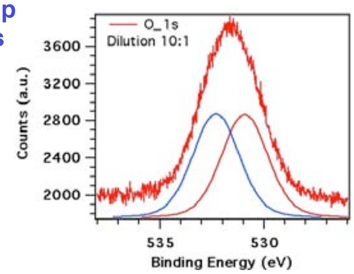
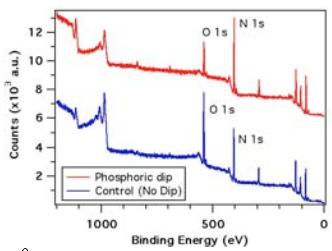
Surface treatment: wet chemistry

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Equilibrium conditions
- HCl dip (6M soln.)
  - no effect on O concentration
- HF dip (10:1 dilution)
  - small OH^- reduction
- H_3PO_4 dip (pH 2 & 3)
  - large O^{2-} reduction

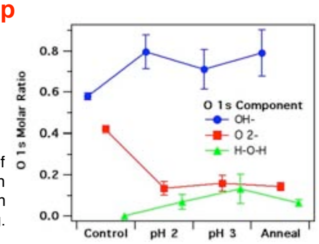
HF dip
O 1s





XPS survey scans of samples before and after H_3PO_4 dip. The O 1s peak intensity decreases.

H_3PO_4 dip
O 1s



Plot of molar ratio of components of the O 1s peak showing decrease in the O^{2-} component and stabilization with respect to annealing.

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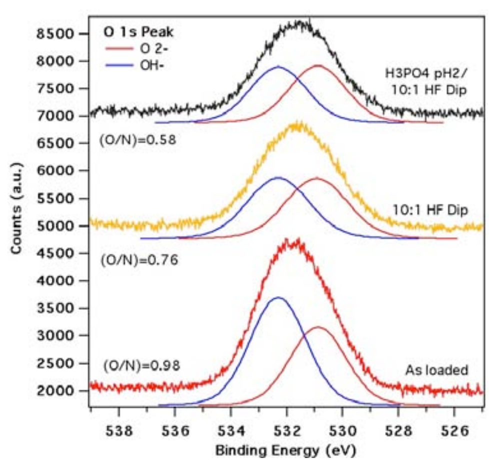
Surface treatment: wet chemistry

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Can oxide components be treated individually?
- Combined effect of H_3PO_4 followed by HF
- Net oxygen removal
- Equilibrium stoichiometry corresponds to HF dip



Mechanism for reduction of thick hydroxide layers

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Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Reproducibly attained smooth high-quality polished surfaces
- Identified the oxide on RT air-exposed AlN surfaces: aluminum oxide hydroxide (AlOOH)
- Analyzed the thermal, hydrothermal evolution of the surface oxide; surface behavior determined by Al
- Estimated the thickness of hydroxide layers
- Studied the effectiveness of wet chemical treatments for hydroxide removal
- Identified a mechanism for reduction of thick hydroxide layers

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Additional research

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- X-ray reflectivity & TEM studies of polished samples for near-surface evaluation
- Investigate *in situ* oxide removal processes compatible with MOCVD
- Homoepitaxial growth of AlN on bulk crystals by MOCVD

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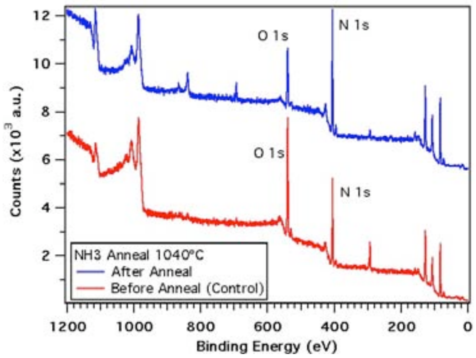
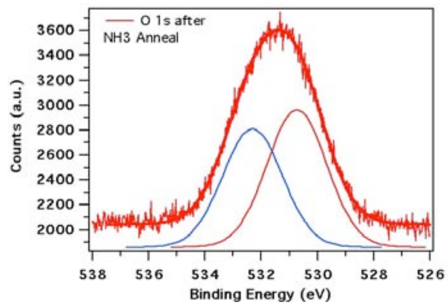
Surface treatment: NH_3 anneal

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- **Ammonia anneal**
  - **T = 1040 ºC**
  - **time = 10 min**
  - **P_{NH3} = 10.5 Torr**

- **Oxygen reduction due to OH^- decrease**



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Is HVPE Fundamentally Inferior to PVT of AlN

Ramon Collazo, Rafael Dalmau, Ziad Herro, Deijin Zhuang, Zlatko Sitar
North Carolina State University

Motivation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

HVPE

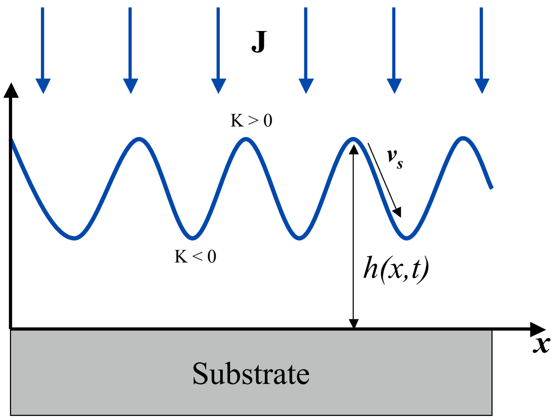
- Low temperature, <1400°C
- Growth rate: 100-200 µm/hr
- Properties
  - Opaque
  - DCRC: 1200 arcsec

PVT

- High temperature, >2200°C
  - material compatibility
  - thermal stress
  - growth control
- Growth rate: 100-500 µm/hr
- Properties
  - Transparent
  - DCRC: 20 arcsec

Evolution of Surface Morphology

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- **Development of surface morphology determined by**
  - **local surface curvature, K**
  - **velocity of species on the surface, v_s**

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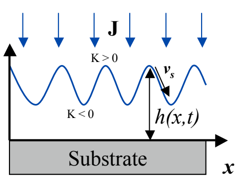
Model of Surface Evolution

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



$$\frac{\partial h(x,t)}{\partial t} = F(x,t) - v_{\perp}(x,t)$$

- **Deposition, *F(x,t)***
  - **Constant incoming flux, *J***
  - **Finite atomic size, δ**
  - **Surface curvature, *K(x,t)***

$$F(x,t) = J + \delta J K(x,t)$$

- **Surface diffusion**
  - **Perpendicular surface velocity due to surface diffusion, $v_{\perp}$**

$$v_{\perp}(x,t) = -D_e \nabla_S^2 K(x,t)$$

$D_e = \frac{D_S \sigma_S \Omega^2 \varepsilon}{k_B T}$; *effective diffusivity*

D_s = *surface diffusivity*

σ_s = *isotropic surface energy density*

Ω = *atomic volume*

ε = *number of atoms perunit area*

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Perturbation Analysis

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

In the small slope limit: $\frac{\partial h}{\partial x} \approx 0$

$$\frac{\partial h}{\partial t} = J - \delta J \frac{\partial^2 h}{\partial x^2} - D_e \frac{\partial^4 h}{\partial x^4}$$

Initial sinusoidal perturbation: sin(kx) and subtracting J

$$h(x,t) = A(t)h(x,0)$$

Surface morphology given by:

$$h(x,t) = e^{\left(\delta J k^2 - D_e k^4\right)t} \sin(kx)$$

- **Non-linear terms in overall equation saturate instability into a relatively small amplitude surface profile.**

λ is the wavelength of the initial perturbation

Unstable mode:

$$\delta J k^2 - D_e k^4 > 0 \xrightarrow{\lambda = \frac{2\pi}{k}} \boxed{\lambda > \lambda_0}$$

where $\lambda_0 = \sqrt{\frac{4\pi^2 D_e}{\delta J}}$

"effective" diffusion length

$\lambda_m = \sqrt{2}\lambda_0$ is the most unstable mode

depends on

- **Substrate**
- **Nucleation**
  - Supersaturation
  - Initial surface preparation

depends on

- **Growth Process (J)**
- **Surface/ Surface Diffusion**

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Process Conditions (λ_0)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

"Effective" diffusion length

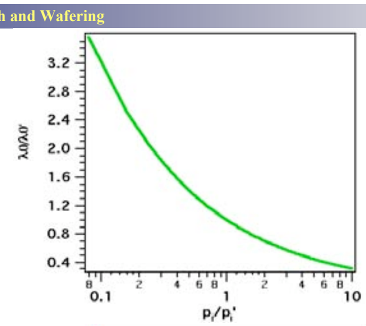
$$\lambda_0 = \sqrt{\frac{4\pi^2 D_e}{\delta J}}$$

- **Limiting reactant specie flux (J)**

$J \propto \Delta p = p_i$ input partial pressure of the limiting reactant. ($p_i >> p_{eq}$)

At a given temperature

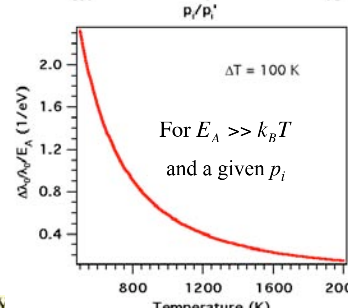
$$\frac{\lambda_0}{\lambda_0'} = \sqrt{\frac{p_i'}{p_i}}$$



- **Temperature (Surface diffusion)**

D_S is the surface diffusion, with a given activation energy E_A. $D_S = D_0 e^{-E_A/k_B T}$

$$\lambda_0 = \sqrt{\frac{Ae^{-E_A/k_B T}}{T}} \rightarrow \frac{\Delta\lambda_0}{\lambda_0} = \frac{(E_A - k_B T)}{2k_B}\frac{\Delta T}{T^2}$$



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Process Conditions (λ)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Nucleation (λ)**

Critical nuclei radius

$$\rho_C \propto \frac{1}{\Delta G_V} = \frac{1}{k_B T \ln(1+\sigma)}$$

$$\approx \frac{1}{k_B T \ln \sigma} \quad \text{with} \quad \sigma >> 1$$

ΔG_V : Process Free Energy Change/ Supersaturation

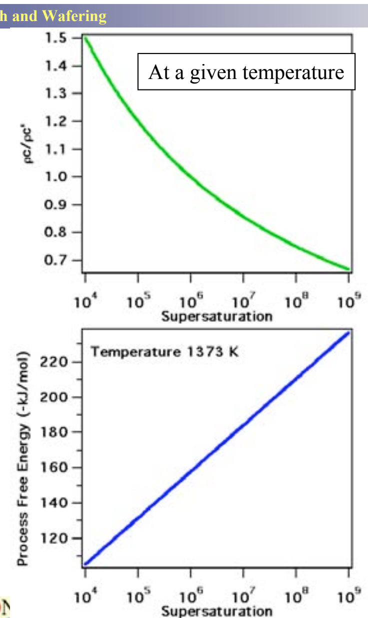
Nuclei density and surface preparation

$$\dot{n} = n^* \omega A^* \text{ where } n^* = n_S \exp\left(-\Delta G^* / k_B T\right)$$

$$\text{and } \Delta G^* \propto \frac{1}{(\Delta G_V)^2} \approx \frac{1}{(k_B T \ln \sigma)^2}, \text{ thus}$$

$$\frac{n^*}{n_S} \propto \exp\left(-\frac{1}{(\ln \sigma)^2}\right)$$

$\dot{n}$: Nucleation rate.
n^* : Equilibrium nucleation density.
ω : atom-nuclei impigement rate.
A^* : nuclei critical area.
n_S : nucleation site density.
ΔG^* : Energy barrier for nucleation.



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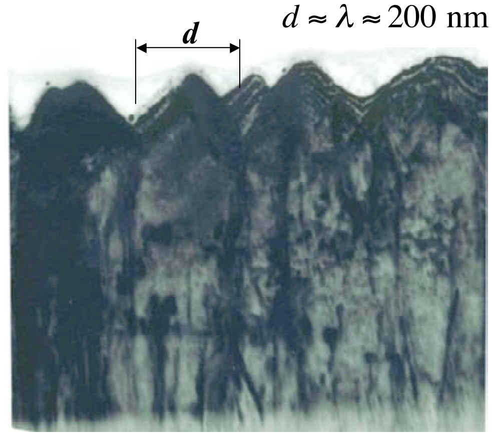
HVPE AlN: Columnar Structure

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

$d \approx \lambda \approx 200$ nm



***d* : grain size**

Dark field TEM micrograph for the [0 0 0 2] direction with zone axis [0 1 -1 0].

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Conclusions

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **HVPE of AlN has fundamental limitations that are manifested in the mosaicity of deposited films and stability of the growth surface**
  - **due to a low growth temperature, the growth surface can be controlled only through the nucleation process and columnar growth**
  - **coalescence of columns into structures wider than the critical surface diffusion distance results in surface roughening and deterioration of crystalline quality**
- **seeded PVT growth of AlN does not suffer from above limitations**

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Physical Modeling of AlN/GaN Vapor Growth

Dang Cai, Xiaolin Wang, Hui Zhang
Department of Mechanical Engineering
State University of New York at Stony Brook

May 08, 2006

Summary of AlN/GaN Growth Simulations

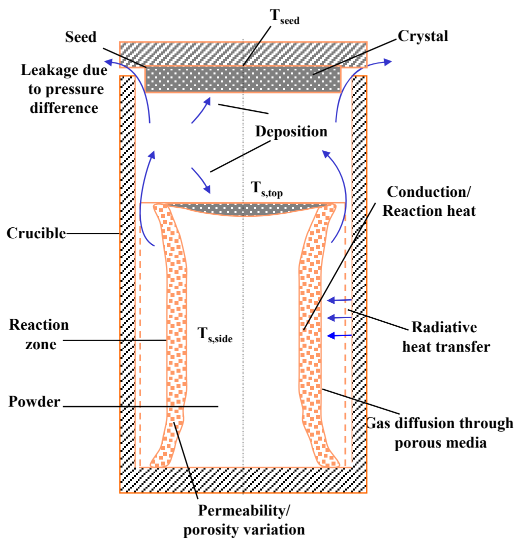
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- AlN Sublimation Growth
  - **Heat and mass transport in AlN sublimation growth;**
  - **Source powder size/porosity, Stefan flow and diffusion controlled flow;**
  - **Isotropic/anisotropic models for vapor deposition process;**
  - **Seed, axial and radial temperature and poly-crystal effects on growth, stresses and defects.**
- GaN IVPE Growth
  - **Optimization of geometrical parameters and operating conditions for fast and uniform GaN IVPE deposition;**
  - **Thermodynamic and kinetic analysis of gas phase/surface reactions in source bubbler and reactor chamber to identify critical reaction steps;**
  - **Quasi-equilibrium and kinetic models developed to predict GaN growth rate.**

Publications: 1 book chapter, 7 journal papers and 14 conference papers

Powder Sublimation & Vapor Deposition

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- **Reaction zone size & movement are controlled by driving force, porosity and permeability.**
- **Driving force is due to the following temperature difference at different locations:**
  - **From source to seed**
  - **From leakage to cold surfaces**
  - **From side to top surfaces**
- **Temperature variation is due to powder decomposition, coupling between source and heater.**

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Powder Sublimation and Porosity Evolution

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Assumptions:

- **Neglecting temperature change**
- **Considering uniform particle size for initial source material**
- **Diffusion only due to low Grashof number & low Stefan flow velocity**

Continuity equation: $\frac{\partial}{\partial t}\left[\rho_s(1-\phi)+\rho_g\phi\right]+\frac{1}{r}\frac{\partial}{\partial r}(r\phi\rho_g u_r)=0$

Reaction equation: $\frac{\partial \rho_s(1-\phi)}{\partial t}=-R_p$

$$\frac{\partial\phi}{\partial t}=\frac{R_p}{\rho_s}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(\phi r u_r)=\frac{R_p}{\rho_g}$$

$$R_p=Z\exp(A-\frac{B}{T})$$

$$u=\frac{K}{\mu}\nabla p$$

$$p=\int\frac{\mu}{K}u_r\,dr$$

Energy Conservation: $(1-\phi)\rho_s C_s\frac{\partial T}{\partial t}+\phi\rho_g u_z C_g\frac{\partial T}{\partial z}=\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(rk\frac{\partial T}{\partial r}\right)-(1-\phi)Q_pR_p$

$$k=\phi(k_{gas}+\frac{32}{3}\varepsilon\sigma T^3 d_p)+(1-\phi)k_{solid}$$

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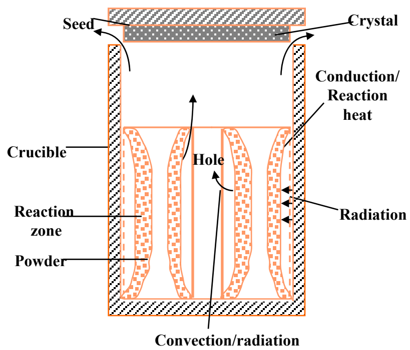
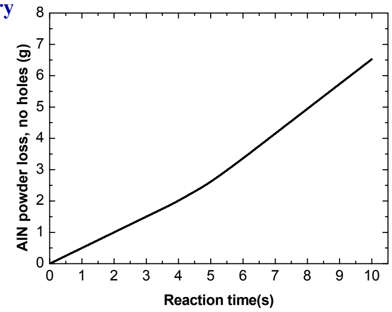
Increase AlN Powder Sublimation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Better understanding of powder porosity and geometry and their impacts on crystal growth rate.
- Optimization of growth conditions by adding holes in the powder.
- Studying the effect of sizes/dimensions of holes on sublimation rate.





Hole size (mm)	Total AlN sublimation increase in presence of a central hole (%)
10	30
18	40

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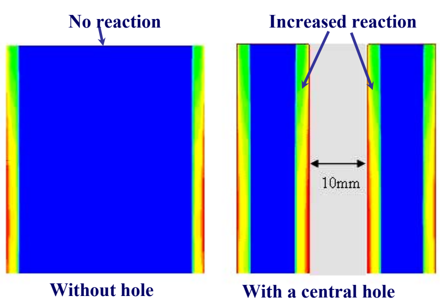
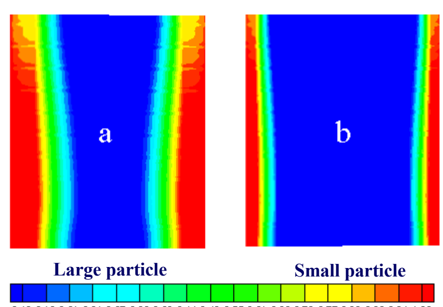
Porosity Evolution

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering





- Initial porosity of 0.1 is used in above cases; powder sublimation time=10 hours.
- AlN sublimation rate can be increased by creating one or several holes in the powder source.
- Effect of AlN particle size: powder sublimation time=50 hours.
- Reaction zone size depends on porosity and permeability. Reaction zone in Fig. (a) is bigger than that in Fig. (b).

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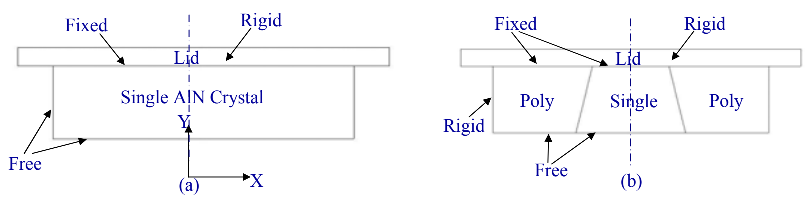
Axi-symmetric Stress Simulation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



Scenario 1	**Axial temperature gradient, 5 °C/mm; and radial temperature gradient, 3 °C/mm**
Scenario 2	**Axial temperature gradient, 5 °C/mm; and radial temperature gradient, 3 °C/mm [soft poly-crystal surrounding single crystal]**
Scenario 3	**Axial temperature gradient, 5 °C/mm; and radial temperature gradient, 3 °C/mm [hard poly-crystal surrounding single crystal]**

- The residual stress distribution in the as-grown AlN layers has been calculated with/without considering the poly-crystal effect.

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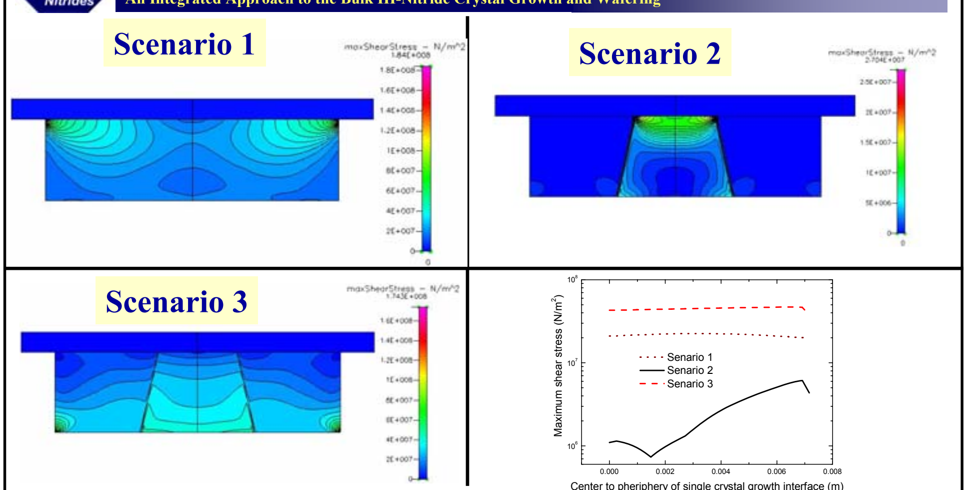
Maximum Shear Stress Distribution

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



- Only a hard polycrystalline material affects the shear stress distribution.
- Stress density is more than doubled on the grown interface of the single crystal when a hard polycrystalline material presents.

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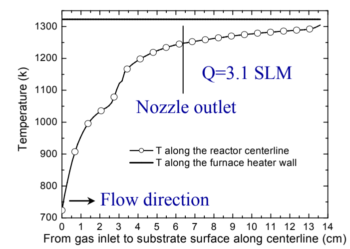
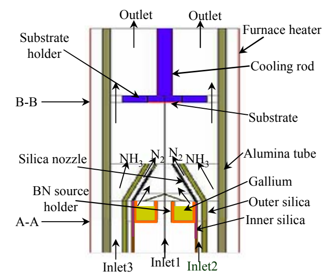
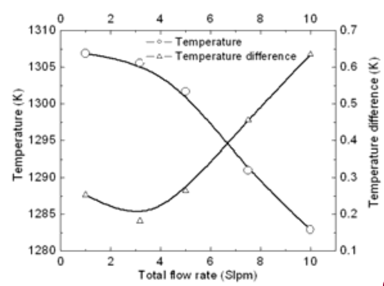
GaN Growth – Effect of Total Flow Rate

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering







- Within a flow rate range of 1-10 SLM, the substrate temperature drops from 1307 to 1283 K.
- A total flow rate of 3 SLM gives the lowest temperature difference, or the best uniformity, on the substrate surface.

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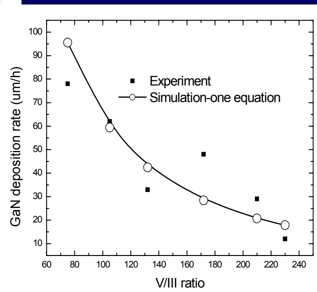
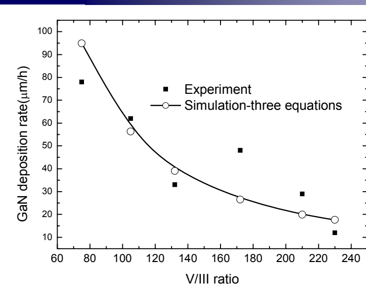
GaN Deposition Model

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



One overall reaction step



Three reaction steps

One Overall Reaction Step	Rate expression (kmol/m^{2}s)
R1 GaI(g)+NH$_3$(g)⇔ GaN(s) +HI(g)+H$_2$(g)	6.5×10^9Exp(-12390/T)[GaI]$^{2.2}$
Three Reaction Steps	Rate expression (kmol/m^{2}s)
R2 GaI(g)+NH$_3$(g)⇔ GaN(s) +HI(g)+H$_2$(g)	0.07Exp(-12390/T)[GaI]
R3 3GaI(g)+2NH$_3$(g)⇔ 2GaN(s) +GaI$_3$(g)+3H$_2$(g)	5.88×10^9Exp(-13630/T)[GaI]^3
R4 GaI$_3$(g)+NH$_3$(g)⇔ GaN(s) +3HI(g)	0.36Exp(-14000/T)[GaI$_3$]

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Deposition Rate and Sticking Probability

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

V/III ratio	GaN deposition rate (μm/h)		Growth rate contribution	
	Reaction R2	Reaction R3	Reaction R2	Reaction R3
75	21.80	73.10	22.97%	77.03%
105	17.62	38.61	31.33%	68.67%
132	15.04	24.01	38.52%	61.48%
172	12.54	13.89	47.41%	52.59%
210	10.86	9.03	54.60%	45.40%
230	10.16	7.40	57.86%	42.14%

V/III ratio	Sticking Probability, S_i		
	GaI ($\times 10^3$)	NH_3($\times 10^6$)	GaI_3($\times 10^3$)
75	2.66	6.50	4.15
105	2.07	4.10	3.12
132	1.75	3.02	2.69
172	1.43	2.08	2.07
210	1.22	1.55	1.86
230	1.13	1.38	1.77

- The contribution of reaction R4 to the deposition rate is found to be less than 0.1% for all cases.
- Sticking probabilities of GaI and GaI_3 are 3 orders of magnitude larger than NH_3.

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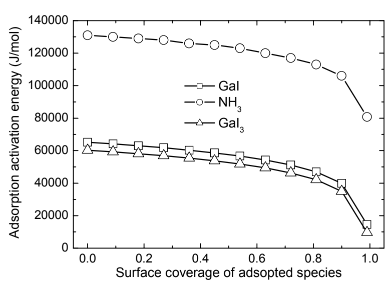
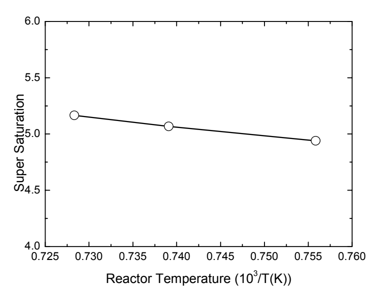
Adsorption Energy and Super-saturation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



$$F(\theta^s)=1-\theta^s$$

The averaged activation energies of adsorption for GaI, NH_3 and GaI_3 by calculation are 5.72×10^4 J/mol, 1.24×10^5 J/mol and 5.28×10^4 J/mol, respectively.



$$\sigma = \ln\left(P_{GaI}P_{NH_3}/P_{HI}P_{H_2}K\right)$$

- The achieved super-saturation is about 5.
- The super-saturation reduces with the temperature slightly, which means that the GaN deposition is diffusion controlled.

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Conclusions

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- AlN powder sublimation model was built, and effect of holes on the powder sublimation was investigated;
- Residual stress distribution in the as-grown AlN layers was studied;
- Temperature and its distribution on the substrate for GaN growth was studied;
- Surface reactions and their rates were determined;
- Sticking probability, species adsorption energy and super-saturation were calculated.

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Bulk GaN crystal growth through Ga vapor transport technique

Huaqiang Wu, Phani Konkapaka, Barry Butterfield
Yuri Makarov*, and Michael Spencer
Cornell University
* STR

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Outline

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- GaN powder decomposition;
- The efficient Ga transport through Ga_2O;
- Improved design to prevent gas phase particles formation;
- Growth rate versus different growth parameter;
- Surface morphology of the grown GaN layer;
- Cracks in the sapphire substrate due to thick GaN layer;
- XRD Characterization of GaN layer;
- Summary

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GaN powder decomposition - I

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Lab made GaN powder has very high purity. Oxygen concentration is less than 400ppm;
- The commercial GaN powder is converted from Ga_2O_3. The powder purity is less than 91% with more than 3% oxygen concentration.
- The very low equilibrium Ga vapor pressure over liquid Ga (several Pascal at 1000°C) limited the total amount transferred out from the GaN powder;
- From thermo dynamical calculations, Ga_2O has much higher vapor pressure and could serve as efficient Ga carrier.
- Ga_2O is unstable and can react with NH_3 to from GaN easily;

	Lab-made powder	Commercial powder
Gas species	N_2, Ga(g)	N_2, Ga(g), GaO(g), Ga_2O(g)
Condensed phases	GaN(s), Ga(l)	GaN(s) Ga_2O_3, Ga(l)
Heterogeneous chemistry	2GaN(s) = 2Ga(s) + N_2(g) Ga(l) = Ga(g)	2GaN(s) = 2Ga(s) + N_2(g) Ga_2O_3(s)+Ga = 3GaO(g) GaO(g) + Ga(g) = Ga_2O(g) Ga(l) = Ga(g)

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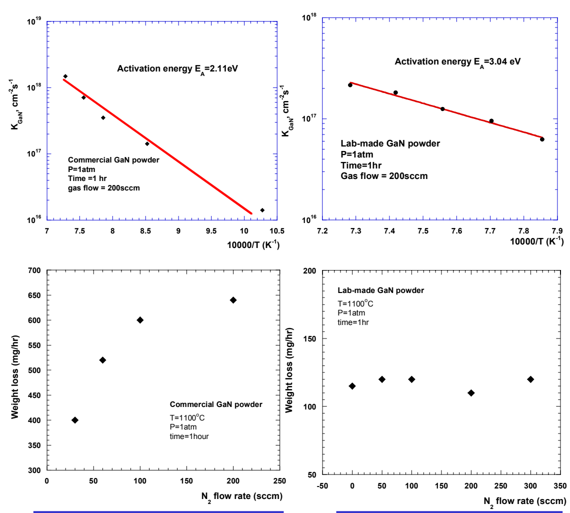
GaN powder decomposition - II

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



Commercial GaN powder

Lab-made GaN powder

➢ Based on the experimental results, the equivalent activation energy of lab-made GaN powder is much higher than the commercial GaN powder. This may due to the lower Ga2O formation and desorption barrier.

➢ The weight loss of commercial GaN powder increase with the carrier gas N_2 flow rate. This provide additional freedom to control the growth. The lab-made powder weight loss is relative independent on the N_2 flow rate.

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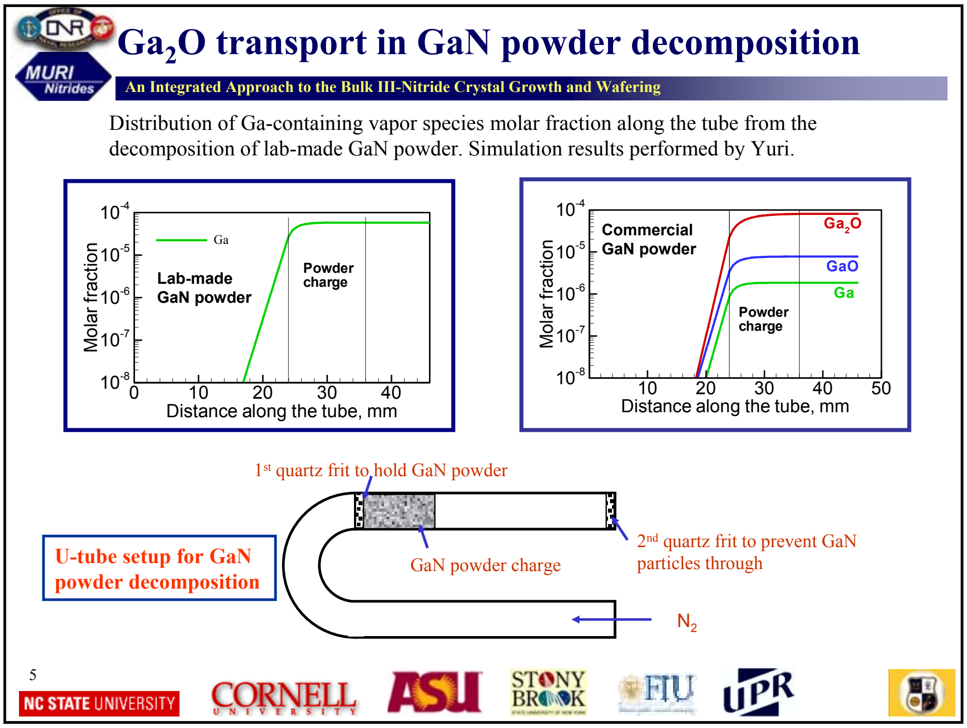
Ga$_2$O transport in GaN powder decomposition
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
Distribution of Ga-containing vapor species molar fraction along the tube from the decomposition of lab-made GaN powder. Simulation results performed by Yuri.
Molar fraction
Ga
Lab-made GaN powder
Powder charge
Distance along the tube, mm
Commercial GaN powder
Ga$_2$O
GaO
Ga
Powder charge
Distance along the tube, mm
1st quartz frit to hold GaN powder
U-tube setup for GaN powder decomposition
GaN powder charge
2nd quartz frit to prevent GaN particles through
N$_2$
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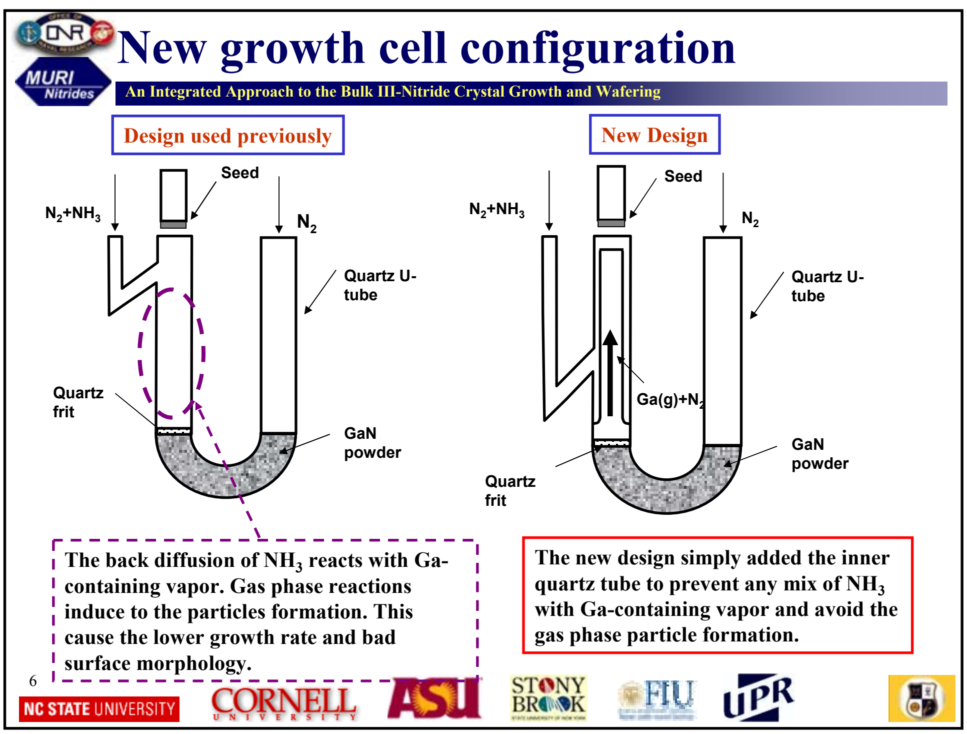
New growth cell configuration
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
Design used previously
New Design
Seed
N$_2$+NH$_3$
N$_2$
Quartz U-tube
Quartz frit
GaN powder
Ga(g)+N$_2$
The back diffusion of NH$_3$ reacts with Ga-containing vapor. Gas phase reactions induce to the particles formation. This cause the lower growth rate and bad surface morphology.
The new design simply added the inner quartz tube to prevent any mix of NH$_3$ with Ga-containing vapor and avoid the gas phase particle formation.
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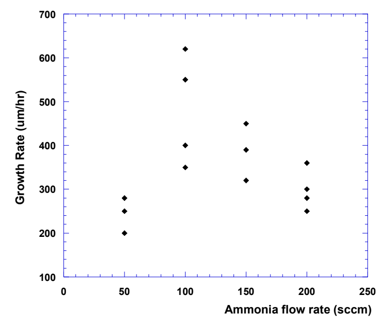
Growth results with new setup

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- About 35 growth experiments have been performed in this design. Repeatable growth results have been achieved with high growth rate.
- Growth rate varies from 200 – (>600) um/hr has been reached.
- Typically, thicker than 150um layer can be obtained after half of hour growth. The sapphire substrate cracked into many pieces after the growth due to the big stress from the thick layer and the substrate.



Seed T=1180°C; Powder T=1110°C;
Substrate-source distance = 5mm;
Growth time: 30minutes;
Carrier gas N_2 flow rate=200sccm;
Total flow rate of ammonia tube: 200sccm. The rest is N_2.

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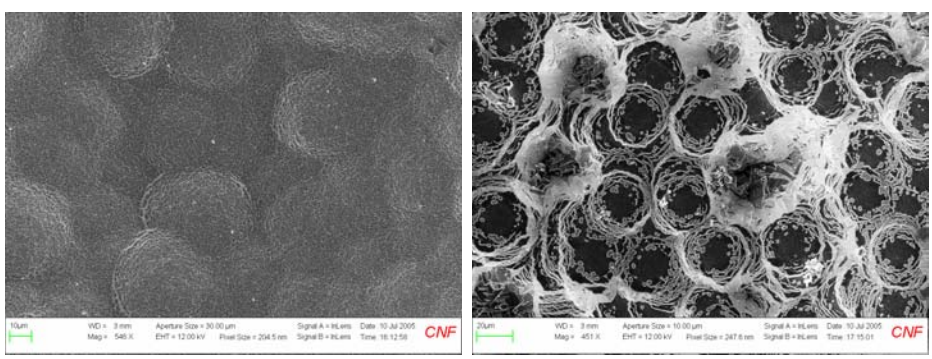
SEM images of surface morphology

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Typical surface morphology of grown GaN layer



- Surface is relatively flat compared to previous design;
- Dominated dislocation shows circular shape;
- The diameter of the circular is about 30um.

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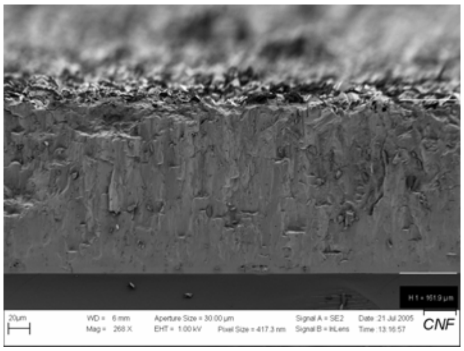
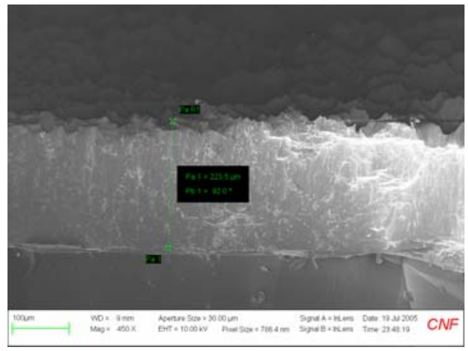
SEM image of cross section

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Cross section view of grown GaN layer





- Cross section SEMs indicate uniform layer on substrate;
- The layer thickness varies from 150um to more than 300um;
- Surface is not flat which might due to particles formation in the cooling down period .

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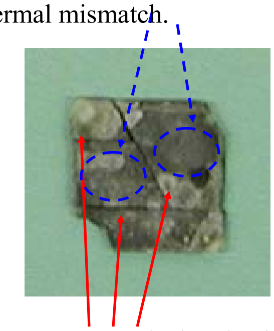
Cracking of seed substrate

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

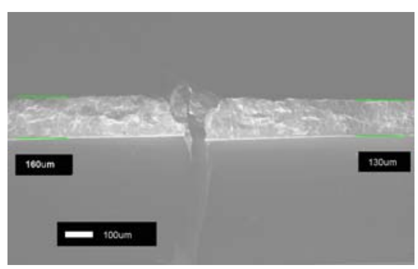
Picture of backside of the sample

Many small cracks originate from the lattice mismatch and thermal mismatch.



Big stress cause the break of the sample. 120o angle crack has been observed.

SEM image of the crack



The crack break both substrate and the grown GaN layer.

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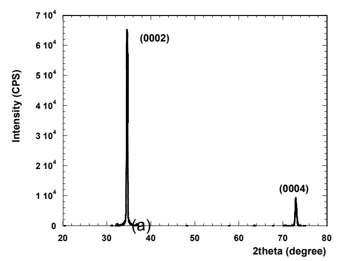
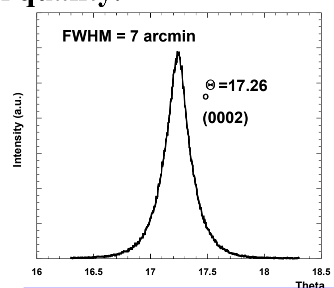
XRD characterization

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **XRD pattern shows the grown GaN layer is single crystal;**
- **FWHM of the XRD rocking curve shows 7 arcmin which is comparable with previous crystal quality.**
- **The new growth setup increase the growth rate dramatically without deteriorating of crystal quality.**



θ-2θ XRD pattern



Double crystal rocking curve of grown GaN layer.

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(b)

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Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Detail experiments have been performed on GaN powder decomposition;**
- **Ga_2O is discovered as the main carrier for Ga-containing vapor transport;**
- **Although lab-made GaN powder has high purity, it is not used for bulk crystal growth due to the low Ga transport ability and liquid Ga formation in the powder source;**
- **New setup has been implemented to prevent gas phase particles formation;**
- **About 35 experimental results from the new design showed much high growth rate and no powder formation originated from the gas phase particles;**
- **As high as 600um/hr growth rate has been reached; growth results are repeatable;**
- **Surface morphology is not good which might come from the cooling period. At that period, the III-V ratio and temperature environment changed and particles formation is preferred.**

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Characterization of AlN and GaN crystals by Synchrotron White Beam X-ray Topography (SWBXT) and High Resolution X-ray Diffraction (HRXRD)

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1

Ammonothermal growth of GaN (AFRL)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Defect Characterization of HVPE GaN seeds prior to ammonothermal growth

- HVPE GaN substrates (from MIT Lincoln Lab (Rich Molnar)) to be used as seeds.
- Defects in seed are usually replicated in the overgrown crystal. Mapping the defect distribution in seeds prior to growth facilitates separation of defects generated during growth from those propagating from the seed in the grown crystal.
- X-ray topographs:
  - Uniform distribution of high density of dislocations (> 10^6/cm^2). Typically, no individual dislocations are resolved.
  - Considerably distorted w.r.t original sample shapes indicating significant lattice plane bending due to residual strains.
- HRXRD measurements:
  - Considerable broadening of rocking curves due to due to a combination of tilt and lattice plane bending is observed.
  - Multiple peaks indicate presence of several subgrains.
  - Triple axis ω-2θ widths vary from 20-40" indicating good quality GaN with low impurities (perfect crystal rocking curve is 10").

Summary of results from HVPE GaN seeds

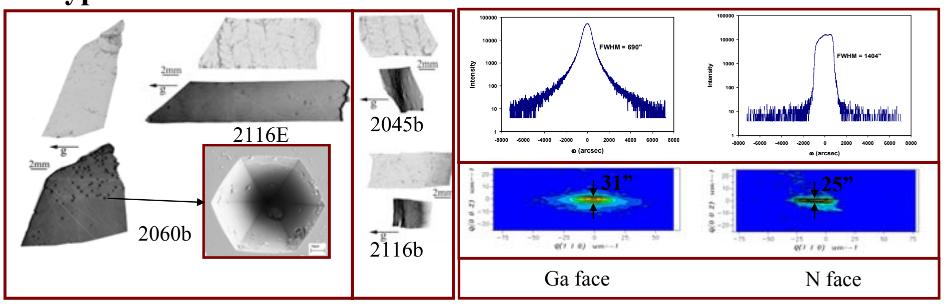
Sample	Ga (growth) face		N (detached) face	
	DCRC (sec)	TCRC (sec)	DCRC (sec)	TCRC (sec)
2045a	1056	32	1282	34
2045b	1060	31	1068	20
2046G	1387	29	1421	20
2046H	1536	25	1477	20
2060a	1121	29	1070	18
2060b	1640	26	1413	23
2060c	1787	29	1447	20
2060d	1798	27	1823	20
2060e	1692	25	1941	18
2109H	497	30	1511	22
2109I	690	31	1404	25
2113G	1423	27	1007	18
2116E	1097	35	1626	35
2116F	780	33	1609	27
2116a	916	34	1036	38
2116b	814	38	1256	25

2

Ammonothermal growth of GaN (AFRL)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

❑ Typical features of HVPE GaN seeds



- ❑ Comparison of optical pictures and corresponding transmission x-ray topographs (g = 11-20) reveals elongation or contraction of topographs depending on direction of bending.
- ❑ Inclusion-like contrast observed on x-ray topographs is actually from hexagonal pits on the Ga growth surface (see: T. Paskova, E. M. Goldys, R. Yakimova, E. B. Svedberg, A. Henry and B. Monemar, JCG, 208 (2000), pp.18-26).
- ❑ Double axis rocking curves recorded from the Ga and N faces exhibit different FWHM widths due to bending in opposite directions.
- ❑ Reciprocal space maps recorded from the N face exhibit somewhat lower triple axis ω-2θ widths than those from Ga face.

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GaN grown from the vapor phase (Cornell)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

❑ Sublimation growth using Ga_2O_3 powders

- Sublimation growth from GaN powders is hindered by formation of liquid Ga in the source, leading to rapidly decreasing growth rates. Further, it is surmised that GaN growth actually occurs by Ga transport in the form of Ga_2O (oxygen present in the source powder).
- Therefore, a new experimental setup to conduct growth using a mixture of Ga_2O_3 and graphite (carbon) powders as the source was designed. At the growth temperature, Ga_2O_3 reacts with carbon to produce Ga_2O which reacts with the ammonia gas to produce GaN.
- Typical growth conditions:
  - Seed temperature – 1100-1200ºC; Source temperature - 1050-1130ºC
  - Pressure - 600 torr; Carrier gas: Nitrogen (450 sccm);
  - Central tube: 10sccm ammonia + 90sccm nitrogen

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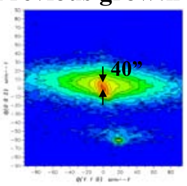
GaN grown from the vapor phase (Cornell)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

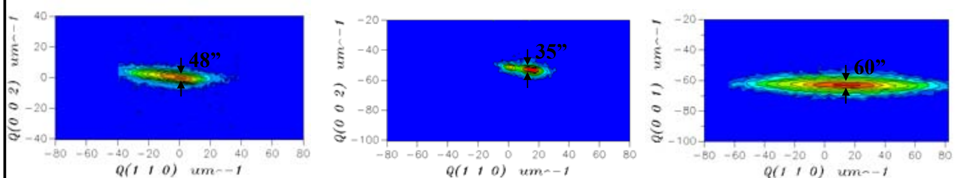
Previous growth runs – best sample



#169

Sample #	DCRC (arcsec)	TCRC (arcsec)
169	**363**	**40**
350	1053	48
351	368	35
352	2825	60

- Reciprocal space maps of layers from previous growth runs reveal tilt and lattice parameter difference between sublimation and epi- grown layers.
- During current runs, the epi and sublimation grown GaN layers are aligned with each other with no tilt or lattice parameter differences (except #351 which shows tilt).
- As indicated by the triple axis ω-2θ widths, the samples vary in quality but generally are similar or slightly better than previous samples.



#350 #351 #352

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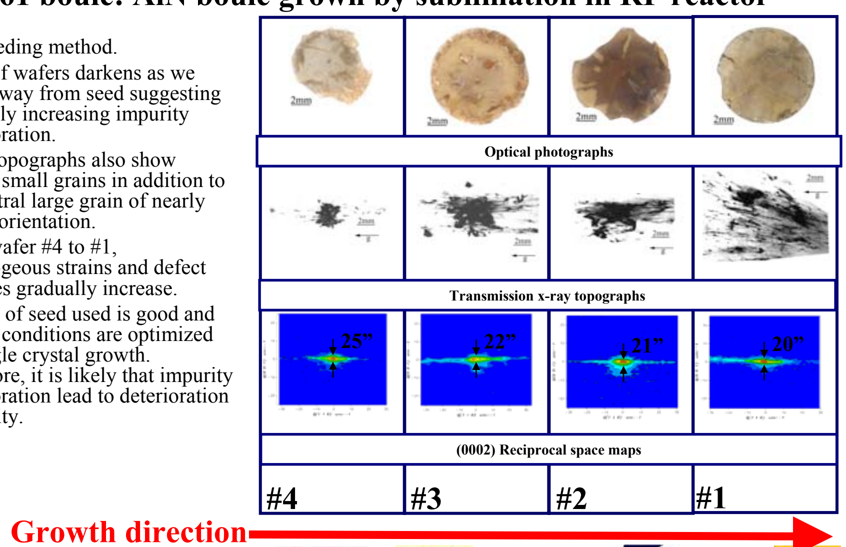
Sublimation growth of AlN (NCSU)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Z-061 boule: AlN boule grown by sublimation in RF reactor

- Self-seeding method.
- Color of wafers darkens as we move away from seed suggesting gradually increasing impurity incorporation.
- X-ray topographs also show several small grains in addition to the central large grain of nearly (0002) orientation.
- From wafer #4 to #1, inhomogeous strains and defect densities gradually increase.
- Quality of seed used is good and growth conditions are optimized for single crystal growth. Therefore, it is likely that impurity incorporation lead to deterioration of quality.



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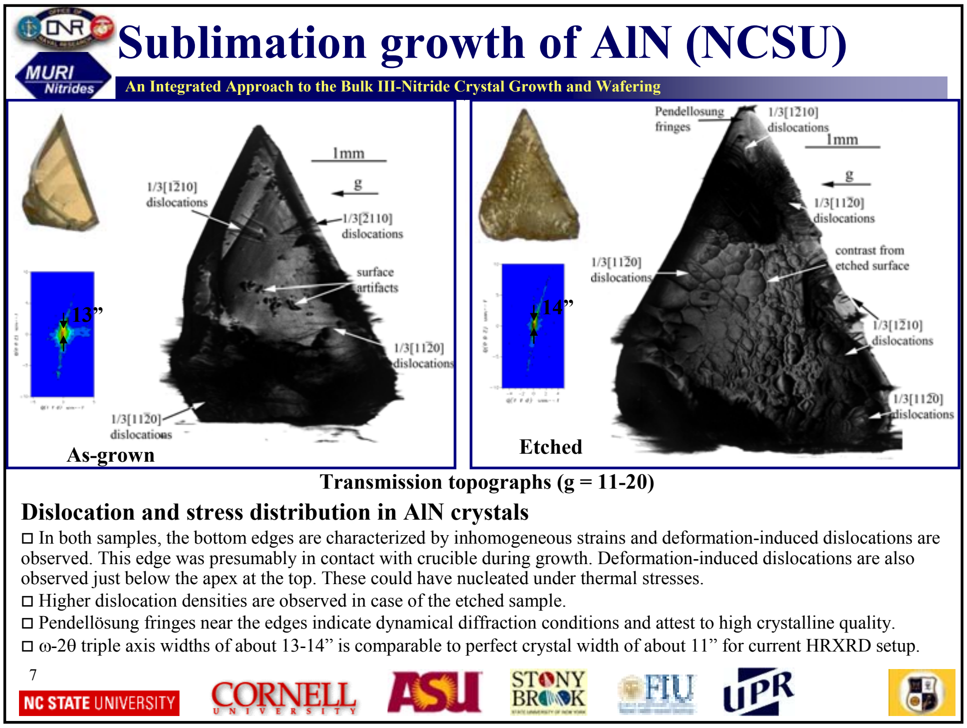
Sublimation growth of AlN (NCSU)
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
MURI Nitrides
1mm
g
$1/3[1\bar{2}10]$ dislocations
$1/3[\bar{2}110]$ dislocations
surface artifacts
$1/3[11\bar{2}0]$ dislocations
$1/3[11\bar{2}0]$ dislocations
13”
As-grown
Pendellosung fringes
$1/3[1\bar{2}10]$ dislocations
1mm
g
$1/3[11\bar{2}0]$ dislocations
contrast from etched surface
$1/3[11\bar{2}0]$ dislocations
14”
$1/3[1\bar{2}10]$ dislocations
$1/3[11\bar{2}0]$ dislocations
Etched
Transmission topographs (g = 11-20)
Dislocation and stress distribution in AlN crystals
□ In both samples, the bottom edges are characterized by inhomogeneous strains and deformation-induced dislocations are observed. This edge was presumably in contact with crucible during growth. Deformation-induced dislocations are also observed just below the apex at the top. These could have nucleated under thermal stresses.
□ Higher dislocation densities are observed in case of the etched sample.
□ Pendellösung fringes near the edges indicate dynamical diffraction conditions and attest to high crystalline quality.
□ ω-2θ triple axis widths of about 13-14” is comparable to perfect crystal width of about 11” for current HRXRD setup.
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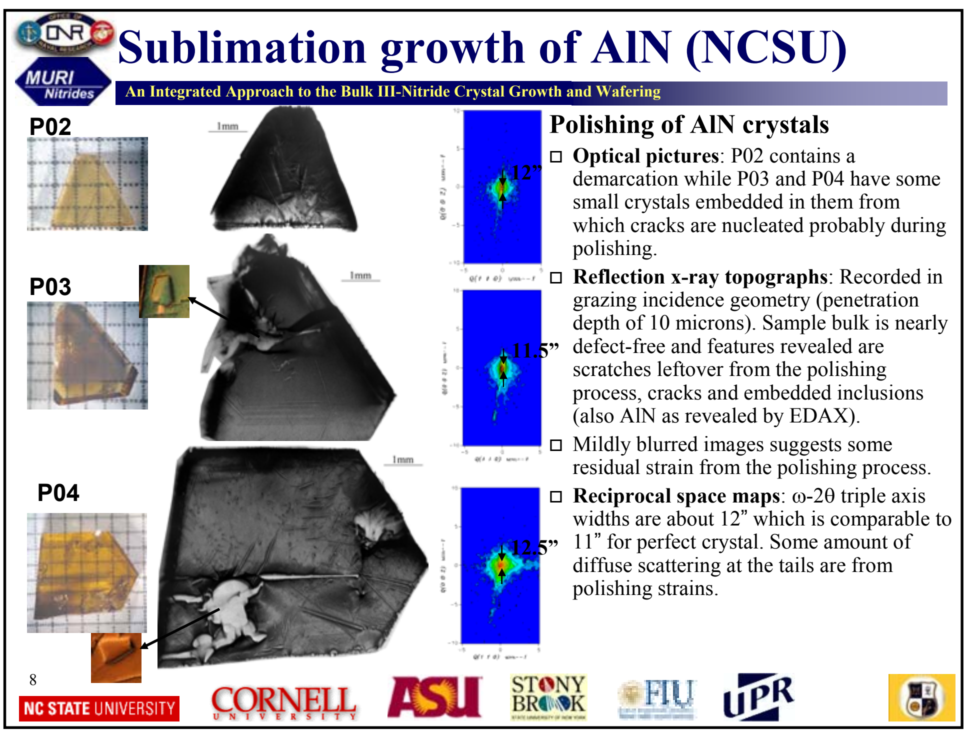
Sublimation growth of AlN (NCSU)
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
MURI Nitrides
P02
1mm
12”
P03
1mm
11.5”
P04
1mm
12.5”
Polishing of AlN crystals
□ Optical pictures: P02 contains a demarcation while P03 and P04 have some small crystals embedded in them from which cracks are nucleated probably during polishing.
□ Reflection x-ray topographs: Recorded in grazing incidence geometry (penetration depth of 10 microns). Sample bulk is nearly defect-free and features revealed are scratches leftover from the polishing process, cracks and embedded inclusions (also AlN as revealed by EDAX).
□ Mildly blurred images suggests some residual strain from the polishing process.
□ Reciprocal space maps: ω-2θ triple axis widths are about 12” which is comparable to 11” for perfect crystal. Some amount of diffuse scattering at the tails are from polishing strains.
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Sublimation growth of AlN (NCSU)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

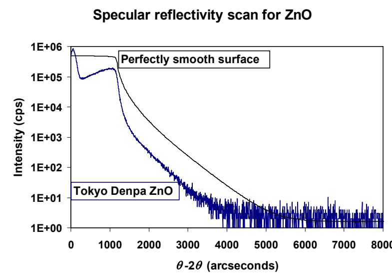
X-ray reflectivity (Grazing incidence X-ray scattering)

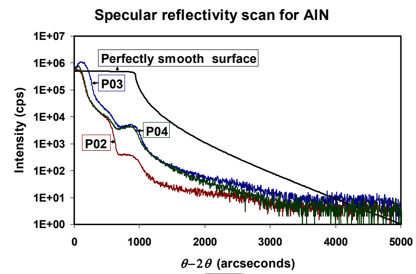
- At small incident angles below some critical angle θ_c, X-rays are totally reflected from solid surface since refractive index for X-rays is less than 1. Above this angle, X-ray beam penetrates the surface successively deeper as the angle is increased and variations in electron density through the sample give rise to distribution of scattered intensity as the incident angle is varied.
- For a non-absorbing, perfectly smooth surface, reflected intensity abruptly falls and is proportional to $(2\theta)^{-4}$ for angles well beyond θc. From rough surfaces, this decline is more rapid.
- Grazing incidence X-ray scattering techniques can be applied to samples with no long-range crystalline order as well as to perfect crystals.
- Thickness of layers upto 1 micron can be determined as well as RMS roughness of surface and interfaces using diffuse scatter.
- For collecting diffuse scatter –
  - Transverse diffuse scatter (fixed detector angle)
  - Longitudinal diffuse scatter (off-specular scan)
  - Detector-only diffuse scatter (fixed sample angle)

- **Requirements: Reasonably flat sample over footprint of beam (else signal will be low) (line focus source preferred).**
- **High intensity beam and wide range detector**

- **For AlN:**
  - **Presence of cracks and embedded inclusions ⇒ surface not flat**
  - **Small sample size ⇒ lower reflected intensity**
  - **Insufficient intensity for proper diffuse scatter measurements**

  ⇒ Optimization of recording conditions is required.





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AlN films grown on sapphire substrates

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Stress evolution during AlN vapor growth

- **#1:** Grown at low temperature with a final thickness of 0.6 µm.
- **#2:** Grown at high temperature with a final thickness of 1.8µm.

Three factors contribute to the state of stress:

- Lattice mismatch: Residual elastic stress $\varepsilon = (N_{substrate} \times d_{substrate} - N_{film} \times d_{film})/N_{film} \times d_{film}$

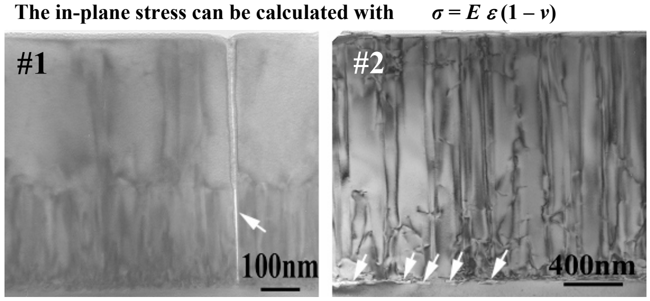
$N_{substrate}$ and N_{film} are measured from HRTEM images

- Coalescence of initial islands: $\varepsilon = \Delta_{max}/L$ $\Delta_{max} = [2L(2\gamma_{sv} - \gamma_{gb})(1 - \nu)/E]$

Parameters are measured from AFM images recorded right before the island coalescence

- Thermal expansion during cooling: $\varepsilon = (\alpha_{film} - \alpha_{substrate})\,\Delta T$

The in-plane stress can be calculated with $\boldsymbol{\sigma = E\,\varepsilon(1 - \nu)}$



Film #1, under tensile stress – tensile crack (mud crack) indicated by arrow;

Film #2, under compressive stress – compressive crack (delamination crack)

(MRS Symp. Proc., 892, FF26-01.1,(2006).

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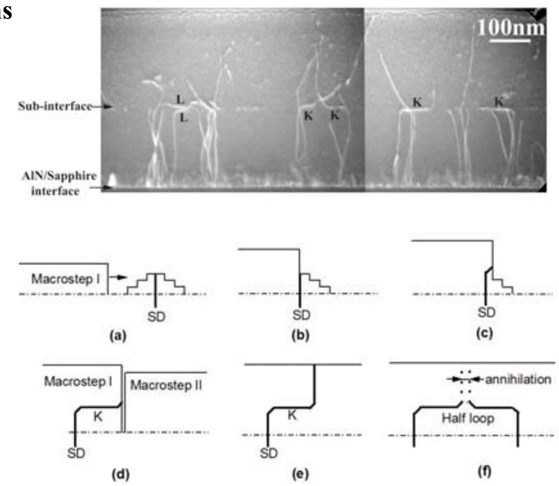
AlN films grown on sapphire substrates

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Bending of threading dislocations driven by growth mode modification

- The V/III ratio was changed to ~11500 and the TMA and NH_3 flow rates were changed to ~9.6 and ~111500 μ mol/min, respectively at the sub-interface.
- Large kinks or dipole half loops formed at the sub-interface.
- Threading dislocation density dropped by a factor of three at the sub-interface.
- The dislocations which experience bending are predominantly of pure screw or mostly screw character.



Reorientation of a screw type TD (J. Bai *et al* APL, 88,051903,2006)

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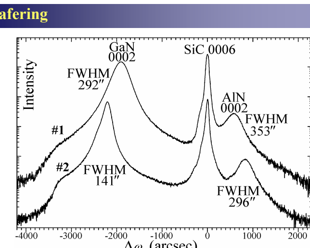
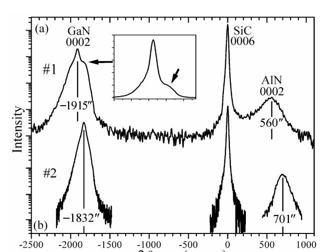
GaN films grown on on-axis and vicinal SiC substrates with AlN buffer

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Sample #1**: on-axis (miscut < 0.1°)
- **Sample #2**: offcut by 3.5°
- FWHM of #2 is only half of that in #1: Vicinal GaN has much higher crystalline quality.
- **Strain relaxation (lower figure):**
  - **Vicinal sample #2**: GaN fully relaxed with a uniform lattice constant. Slight compression in AlN
  - **On-axis sample #1**: GaN with compressive strains and graded lattice constants. The compressive strain of AlN is three times that of #2.
- Advantage of VSE: Higher crystalline quality, facilitating rapid and smooth strain relaxation at the interface (X. Huang at al PRL, 95, 086101-1 (2005); APL, 86, 211916, (2005)).



Double-axis rocking curves of on-axis sample (#1) and vicinal sample (#2) - quite different!



Triple-axis rocking curves (d-spacing scans)

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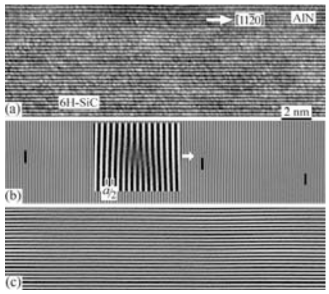
GPMD-driven Strain Relaxation Mechanisms in the vicinal system

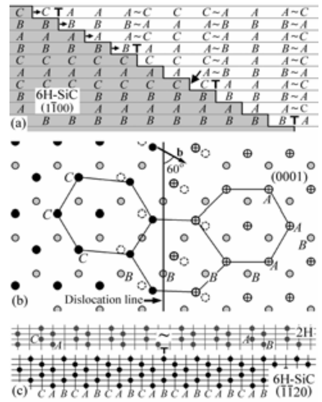
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



High resolution TEM and reconstructed FFT images of the AlN/6H-SiC interface

- **GPMD: Geometrical partial misfit dislocation**

  GPMDs accommodate the lattice mismatch and stacking sequence mismatch simultaneously! More energetically favorable.
- Practical importance: Offcut angle determines step density, the latter determines GPMD density. So by optimizing the offcut angle one can let the GPMDs alone fully relax mismatch without the formation of other defects.
- Theoretical optimal offcut angles:
  - AlN/6H-SiC: 2.8° (Δa/a = 1%)
  - GaN/6H-SiC: 9.7° (Δa/a = 3.5%)



(a) Formation of GPMDs at 2H/6H interface steps. (b) Gradual transition of the stacking sequence of a 60° GPMD connecting the *A* and *C* stacking layers on a *B* layer. Dashed circles represent the original stacking positions without deformation. (c) "Symbol change" above a GPMD with no vertical boundary.

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Overview of Results

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Ammonothermal grown GaN single crystals:**
  - A series of HVPE GaN substrates to be used as seeds for ammonothermal growth have been systematically studied to map their defect distributions in order to facilitate separation of defects due to growth from defects due to propagation from seed.
- **GaN layers grown from the vapor phase:**
  - Several samples grown using the new experimental setup with Ga_2O_3 source have been characterized.
  - Growth optimization has eliminated the tilt and lattice parameter differences between sublimation and epi layers.
- **AlN boule grown from seed in RF reactor:**
  - Gradual increase in defect densities and inhomogeneous strains during growth suggest an increasing impurity incorporation.
- **Polishing of AlN crystals**
  - A combination of SWBXT, HRXRD, AFM and x-ray reflectivity has been used to analyze the polished surface of AlN crystals. Surfaces are characterized by some scratches and mild residual strains.
- **AlN films grown on sapphire substrates**
  - Bending of screw dislocations driven by growth mode modification leads to mutual annihilation and reduction in threading dislocation density.
- **GaN films grown on on-axis and vicinal SiC substrates with AlN buffer**
  - GPMDs accommodate the lattice mismatch and stacking sequence mismatch simultaneously. By optimizing the offcut angle, GPMDs alone fully relax mismatch without the formation of other defects. Optimal offcut angles have been theoretically determined for AlN and GaN on 6H-SiC.

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Work plan for next 6 months

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Ammonothermal grown GaN single crystals (Hanscom):

- ❑ Structural defect characterization of ammonothermal layers grown on HVPE GaN crystals (already characterized by SWBXT and HRXRD).
- ❑ SEM and TEM studies of cross-sectional samples to investigate the nature of the interface (impurities, voids, presence of oxide layer, etc.) and defect generation and propagation.

GaN layers grown from the vapor phase (Cornell):

- ❑ Continued structural characterization of GaN layers grown from Ga_2O_3 source under different growth conditions to further optimize conditions for growing high quality layers.

AlN grown from the vapor phase (NCSU):

- ❑ Detailed characterization of wafers sliced from AlN boules and correlation with growth conditions as well as modeling predictions.
- ❑ Evaluation of polished AlN samples using a combination of SWBXT, AFM and grazing incidence x-ray scattering.

❑ Systematic study of the relationship between the quality of GaN epifilms and the off-cut conditions of the substrate (both SiC and sapphire) using HRTEM, HRXRD and strain modeling.

❑ For GaN samples: Correlation of X-ray and TEM observations with PL measurements (from Prof. Skromme).

❑ For AlN samples: Correlation of HRXRD results with reflectance measurements (from Prof. Skromme).

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MURI Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Identification of Inversion Domain Boundaries in AlN Layers and their Influence on Optical Properties

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Tempe, AZ 85287-6006

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Outline

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Introduction
- Properties and microstructures of AlN layers
- Identification inversion domain boundaries (IDBs)
- Optical properties
- Summary

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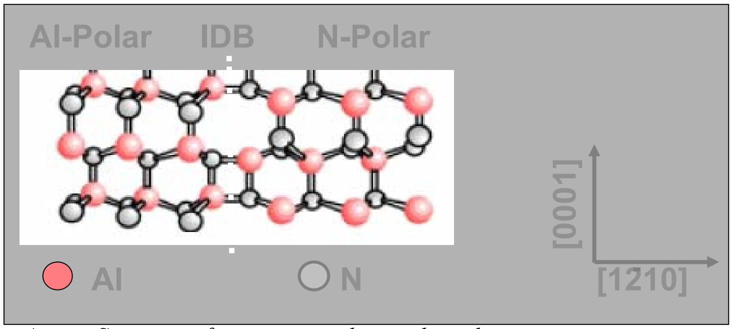
Introduction

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Structure of an IDB



Atomic Structure of an inversion domain boundary

- Schottky barrier height on group III-polar surface is higher and leakage current is lower
- Photoluminescence properties of group V-polar films grown by MOCVD are better than group III-polar films

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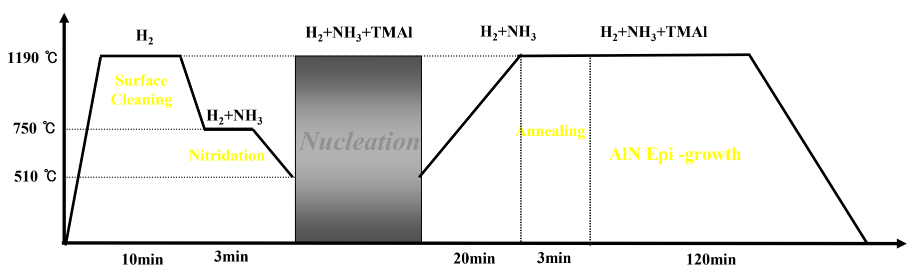
Properties and Microstructures

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Growth Protocol



Summary of the growth process used for AlN deposition

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Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Growth Conditions

Set Ⅰ		Set Ⅱ	
Sample ID	Condition	Sample ID	Condition
031114B	460˚C 1min	040123A	510˚C 15sec
031108B	510˚C 1min	040127A	510˚C 30sec
031105A	560˚C 1min	031108B	510˚C 60sec
031022B	670˚C 3min	040113A	510˚C 90sec
031029A	890˚C 7min	031214B	510˚C 120sec

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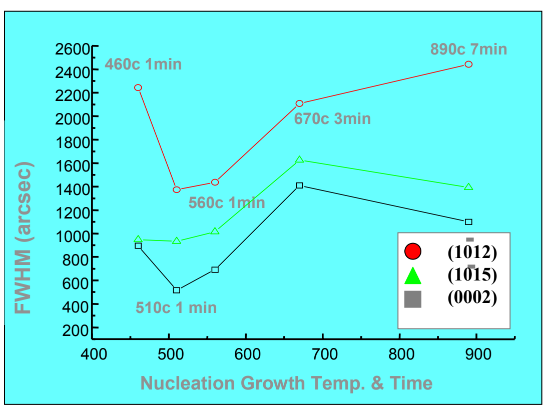
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **XRD FWHM**



XRD FWHM of AlN films as a function of NL growth temperature and time

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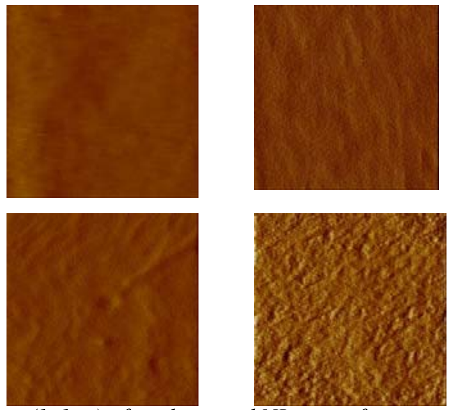
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Surface Morphology of Nuclealzon Layers



AFM images(1x1㎛) of as-deposited NLs as a function of nucleation temperatures (a) 460℃ (b) 510℃ (c) 560℃ (d) 670℃

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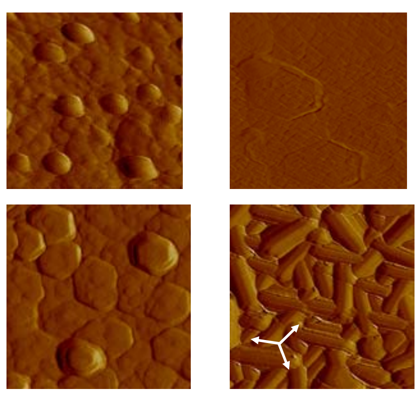
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Surface Morphologies of Overlays



AFM images(1x1㎛) of AlN overlayer as a function of nucleation temperatures (a) 460℃ (b) 510℃ (c) 560℃ (d) 670℃

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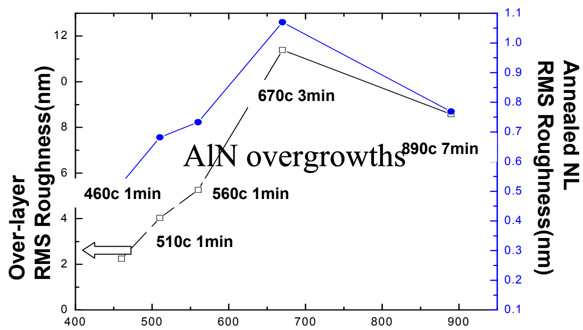
Properties and Microstructures (cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

☐ Surface Roughness of Overlayers



RMS roughness of annealed NLs as a function of growth temperature and AlN overgrowths

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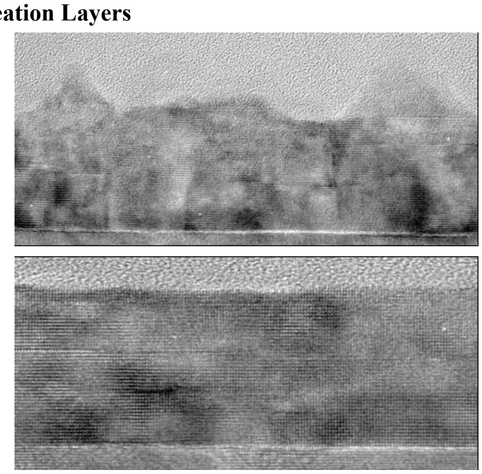
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

☐ IDBs in Nucleation Layers



Cross-sectional HREM images HT AlN growth for 5min on annealed (a) 670℃ 3min NL, (b) 510℃ 30sec NL

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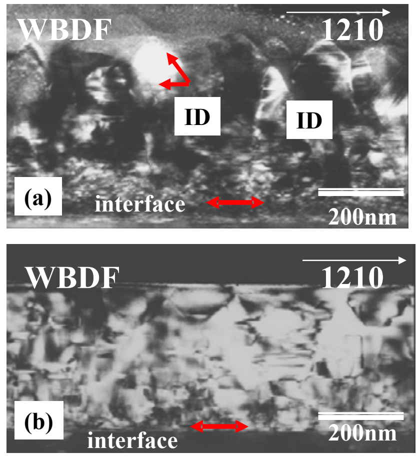
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- IDBs in Overlayers



WBDF images HT AlN growth for 2hours on annealed (a) 670℃ 3min NL, (b) 510℃ 30sec NL

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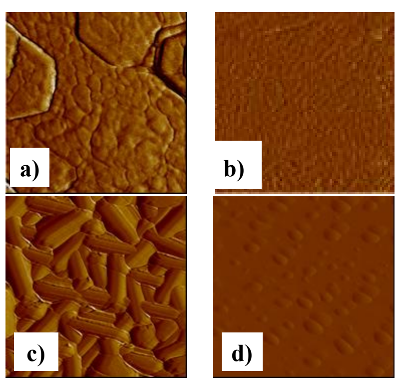
Properties and Microstructures (Cont'd_

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- KOH Etching Response of Overlayers



AFM images (a) as grown and (b) etched AlN on 510℃ 30sec NL (c) as grown and (d) etched AlN on 670℃ 3min NL

•RMS roughness changes from 1.69 in (a) to 0.98 nm in (b)

•RMS roughness changes from 11 nm in (c) to 5 nm in (d)

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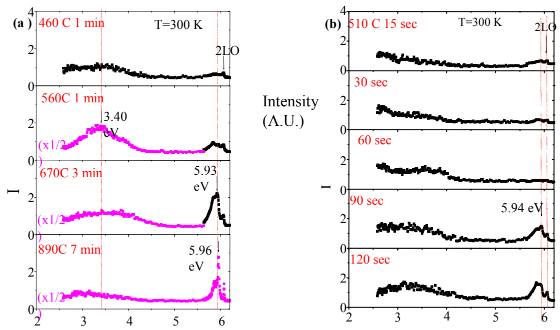
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Photoluminescence Characteristics at 300K**



Photoluminescence spectra (at 300K) from the AlN layer of various conditions. (a) set I (b) set II

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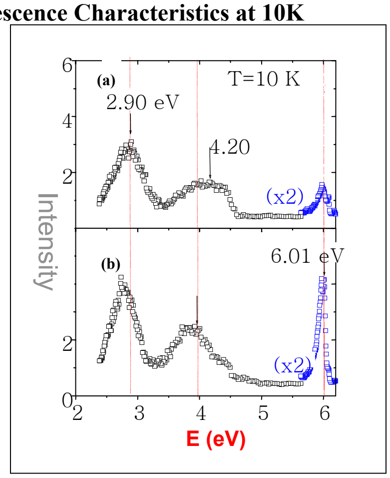
Properties and Microstructures (Cont'd)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Photoluminescence Characteristics at 10K**



Photoluminescence spectra (at 10K) from the AlN layer on (a) 510℃ 30sec NL (b) 670℃ 3min NL

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Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Nucleation layer growth conditions influence the formation of IDBs in AlN
- IDBs can be identified by chemical etching
- Presence of IDBs enhances band-edge emission in AlN layers.

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